STOPPING
WATER POLLUTION
AT ITS SOURCE

MISA
Municipal/Industrial Strategy for Abatement

MISA LABORATORIES

QUALITY ASSURANCE & ANALYTICAL METHODS WORKSHOP

PROCEEDINGS

QD
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Q35
M57
1989
MISA
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Ontario Environment
Environnement
Jim Bradley, Minister/ministre

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PROCEEDINGS/PRESENTATIONS

FROM

MISA LABORATORIES

QUALITY ASSURANCE AND

ANALYTICAL METHODS WORKSHOP

NOVEMBER 28 - 29, 1989

AMMT

INDEX

SECTION ONE	-	Introduction
	-	Topic Abstracts
SECTION TWO	-	Analytical Methods
SECTION THREE	-	Data Management
SECTION FOUR	-	Quality Management
SECTION FIVE	-	Work Group Reports
SECTION SIX	-	List of Participants

SECTION ONE

INTRODUCTION

THE ENVIRONMENT ONTARIO, LABORATORY SERVICES BRANCH WORKSHOP HELD DURING NOVEMBER 28-29TH, 1989 PROVIDED THE OPPORTUNITY FOR LABORATORY TECHNICIANS, SCIENTISTS AND MANAGERS TO PRESENT AND EXCHANGE INFORMATION RELATED TO THE ANALYTICAL SUPPORT OF ONTARIO'S MUNICIPAL/INDUSTRIAL STRATEGY FOR ABATEMENT (MISA) PROGRAM.

OVER THE 2 DAY WORKSHOP, THROUGH FORMAL PRESENTATIONS, SMALL WORKGROUPS FOLLOWED BY AD-HOC PRESENTATIONS BY PARTICIPANTS AND OPEN DISCUSSION, A LOT OF INFORMATION AND IDEAS WERE TABLED.

AS A FOLLOW UP TO THE WORKSHOP, AND AS A MEANS OF A CAPTURING MOST OF THE INFORMATION PRESENTED, THIS PROCEEDINGS/-PRESENTATIONS DOCUMENT WAS COMPILED.

THESE PROCEEDINGS PROVIDE HARD COPIES OF INFORMATION PRESENTED, AND IN MOST CASES, IN THE EXACT FORMAT (SLIDES, OVERHEADS) USED BY THE AUTHORS. THIS WAS DONE INTENTIONALLY TO PROMOTE FURTHER USE AND DISCUSSION BY WORKSHOP ATTENDEES. PLEASE FEEL FREE TO COPY AND USE ANY PORTIONS YOU FEEL WOULD BE BENEFICIAL TO YOUR COLLEAGUES AND STAFF.

IN ADDITION, THESE PROCEEDINGS INCLUDE A SUMMARY REVIEW OF THE AD-HOC WORKGROUPS REPORTS CATEGORIZED AS: TOPICS DISCUSSED; MAIN POINTS OF RESOLUTION OR AGREEMENT AND MAJOR POINTS OUTSTANDING OR REQUIRING ATTENTION. THESE INSIGHTS INTO THE CONCERNS OF LABORATORY STAFF ALONG WITH THE RESULTS OF THE WORKSHOP QUESTIONNAIRE (A SUMMARY REVIEW OF WHICH IS INCLUDED HERE) WILL BE USED TO SHAPE AND FOCUS FUTURE MINISTRY WORKSHOPS.

ON BEHALF OF ENVIRONMENT ONTARIO LABORATORY SERVICES BRANCH, MANAGEMENT AND STAFF, THANK YOU FOR YOUR ATTENDANCE AND INTEREST.

G. CRAWFORD
MANAGER, TRACE ORGANICS SECTION
AND QUALITY ASSURANCE
LABORATORY SERVICES BRANCH
FEBRUARY 1990

ENVIRONMENT ONTARIO

MISA Laboratories Quality Assurance and Analytical Methods Workshop Questionnaire

November 28th and 29th, 1989
Toronto Airport Hilton International

PLEASE ASSIST US IN PLANNING FOR FUTURE WORKSHOPS BY COMPLETING THIS QUESTIONNAIRE AND HANDING IN PRIOR TO YOUR DEPARTURE.

	Very Good	Good	Adequate	Poor	No Comment
1. Quality of Presentations:					
A) How did you find the quality of presentations?	20%	65%	11%	-	4%
B) What was the value of the information presented?					
Session I	20%	59%	17%	-	4%
Session II	8%	55%	27%	4%	6%
Session III	32%	46%	8%	-	13%
C) Please rate the timing of individual presentations.					

COMMENTS: _____

_____

2. Format of Workshop:					
A) Were the large sessions useful?	10%	54%	27%	2%	7%
B) Were the individual sessions useful?	22%	44%	28%	4%	2%
C) Your overall assessment of the Workshop	9%	62%	17%	<1%	10%

COMMENTS: _____

_____

3. Quantity of Information:					
A) Did the Workshop answer your needs?	6%	42%	42%	4%	6%

	Very Good	Good	Adequate	Poor	No Comment
B) Please rate your impression of overall volume of information versus time.	8%	50%	32%	2%	8%
4. Performance Management of Laboratories:					
A) How well did this Workshop address this issue?	16%	42%	22%	-	10%
B) How well does MOE respond to your enquiries on:					
- methods	8%	46%	20%	6%	10%
- regulations	8%	50%	19%	2%	12%
- quality management	8%	52%	20%	3%	8%
5. How well were the following topics addressed:					
A) Conventionals	4%	44%	28%	2%	12%
B) Inorganics	2%	34%	30%	1%	33%
C) Organics	1%	31%	23%	2%	53%
D) Elemental Characterization	2%	21%	23%	3%	52%
E) Organic Characterization	4%	17%	27%	1%	51%
F) Data Management	5%	40%	25%	3%	27%
G) Low Level Data Management	6%	36%	24%	5%	29%
H) Ministry Policy/Protocols	8%	40%	24%	1%	26%
7) What is your overall assessment of this Workshop?	12%	58%	19%	-	10%

6. What are your two top priority areas <u>not</u> addressed in this Workshop?_____

_____

<u>Optional</u>

Name:_____

Affiliation:_____

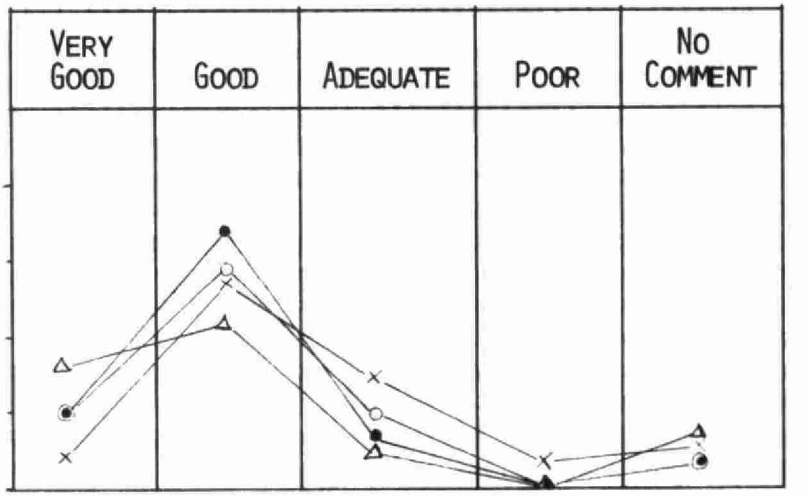
Telephone:_____

ENVIRONMENT ONTARIO

MISA Laboratories Quality Assurance and Analytical Methods Workshop Questionnaire

November 28th and 29th, 1989
Toronto Airport Hilton International

PLEASE ASSIST US IN PLANNING FOR FUTURE WORKSHOPS BY COMPLETING THIS QUESTIONNAIRE AND HANDING IN PRIOR TO YOUR DEPARTURE.



1. QUALITY OF PRESENTATIONS:

   A) HOW DID YOU FIND THE QUALITY OF PRESENTATIONS? •

   B) WHAT WAS THE VALUE OF THE INFORMATION PRESENTED?

      SESSION I ○

      SESSION II ×

      SESSION III △

   C) PLEASE RATE THE TIMING OF INDIVIDUAL PRESENTATIONS.

COMMENTS: _____

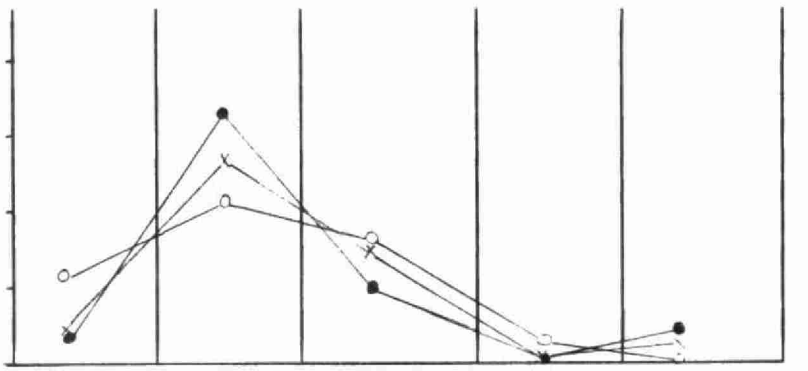
_____

2. FORMAT OF WORKSHOP:

   A) WERE THE LARGE SESSIONS USEFUL? ×

   B) WERE THE INDIVIDUAL SESSIONS USEFUL? ○

   C) YOUR OVERALL ASSESSMENT OF THE WORKSHOP •



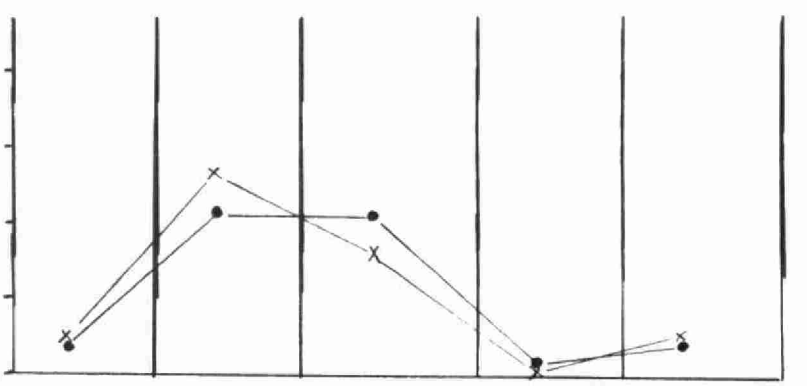
COMMENTS: _____

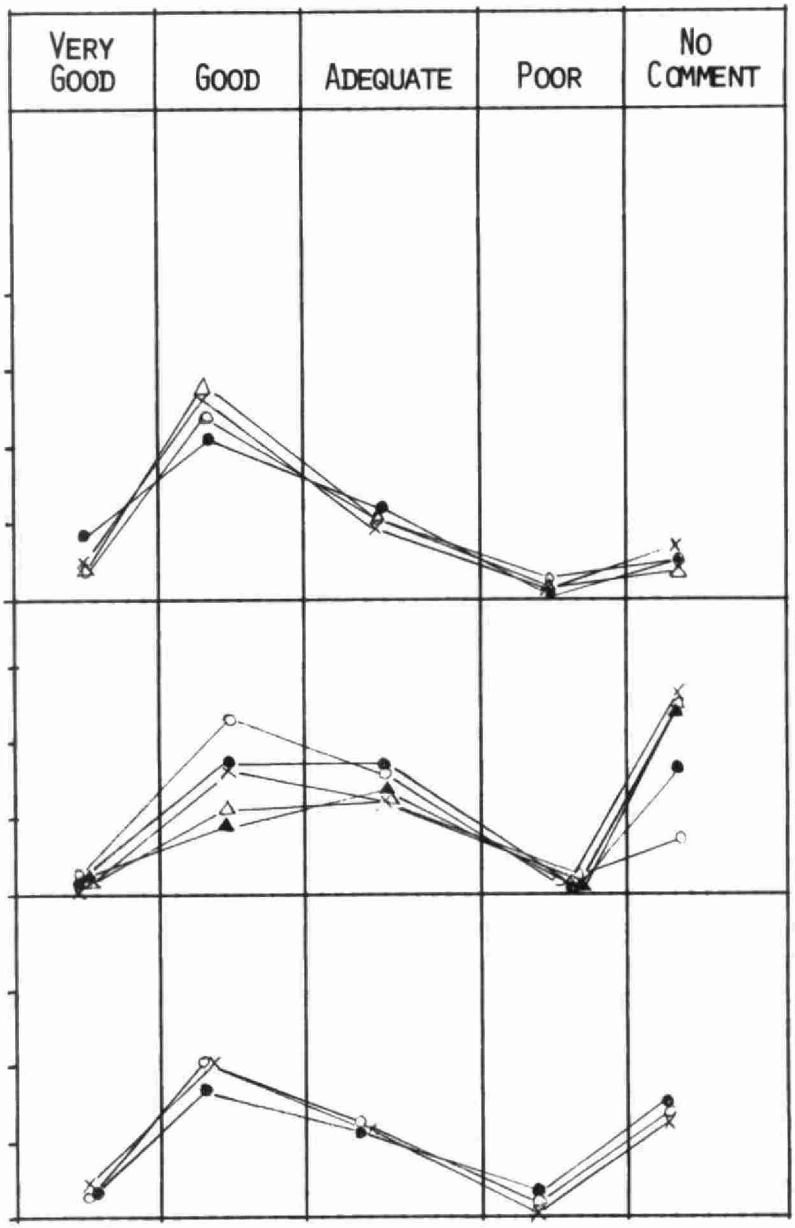
_____

3. QUANTITY OF INFORMATION:

   A) DID THE WORKSHOP ANSWER YOUR NEEDS? •

   B) OVERALL VOLUME OF INFO VS. TIME ×





4. PERFORMANCE MANAGEMENT OF LABORATORIES:

   A) HOW WELL DID THIS WORKSHOP ADDRESS THIS ISSUE? ●

   B) HOW WELL DOES MOE RESPOND TO YOUR ENQUIRIES ON:

      - METHODS ○
      - REGULATIONS ×
      - QUALITY MANAGEMENT △

5. HOW WELL WERE THE FOLLOWING TOPICS ADDRESSED:

   A) CONVENTIONALS ○

   B) INORGANICS ●

   C) ORGANICS ×

   D) ELEMENTAL CHARACTERIZATION △

   E) ORGANIC CHARACTERIZATION ▲

   F) DATA MANAGEMENT ○

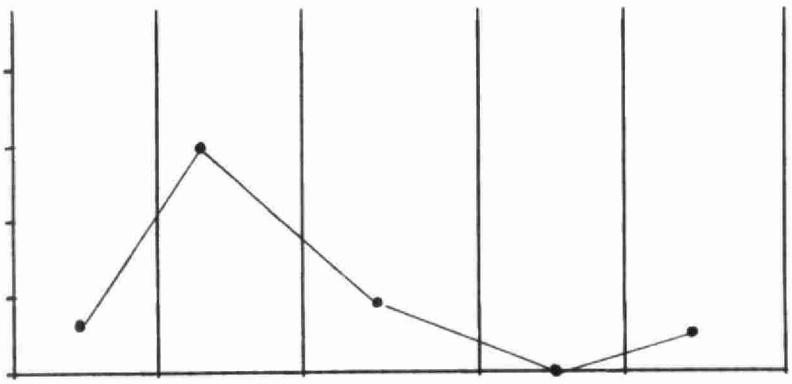
   G) LOW LEVEL DATA MANAGEMENT ●

   H) MINISTRY POLICY/PROTOCOLS ×

6. WHAT ARE YOUR TWO TOP PRIORITY AREAS NOT ADDRESSED IN THIS WORKSHOP?_____

_____

7) WHAT IS YOUR OVERALL ASSESSMENT OF THIS WORKSHOP? ●



OPTIONAL

NAME:_____

AFFILIATION:_____

TELEPHONE:_____

MISA LABORATORIES' QUALITY ASSURANCE AND ANALYTICAL METHODS WORKSHOP

November 28th and 29th, 1989
TORONTO AIRPORT HILTON INTERNATIONAL
MISSISSAUGA ROOM

SPEAKER ABSTRACTS

SESSION ONE ooo ANALYTICAL METHODS

A) Regulatory Overview

Wendy S. Moss, MOE/Laboratory Services Branch

The legal requirements for laboratory analysis of MISA samples, as specified in the General Regulation will be presented. Both textual and Schedule 3 requirements will be covered.

B) MOE Methods Co-ordination

Cammy Raposo, MOE/Laboratory Services Branch

Environment Ontario's Laboratory Services Branch has available their analytical procedures which meet the MISA regulation requirements. Their availability, as well as an overview of the process for their documentation and approval will be presented.

C) Evaluating New Instrumental Measurement Methods - NIMMP

Peter Campbell, MOE/Laboratory Services Branch

The MISA Monitoring Regulations specify Instrumental Measurement Method Principles (IMMP) in Schedule 3. MOE supports and encourages the search for new IMMP (NIMMP) which may reduce analytical costs or provide more reliable or more comprehensive data. The procedure for proposal and approval of NIMMP for future MISA regulations will be introduced.

D) MDL Protocols/Calculation

Don King, MOE/Laboratory Services Branch

The MISA program protocol for calculating analytical method detection limits (MDL) will be reviewed, along with the purpose and statistical basis for the use of MDL.

SESSION TWO ooo DATA MANAGEMENT

A) Low Level Data Reporting

Don King, MOE/Laboratory Services Branch

The general protocols for reporting or censoring low level data will be detailed, including the use of remark codes in the MISA Data Entry System (MIDES) to qualify data for matrix related problems.

B) MISA Data Entry System - MIDES

Don Weatherbe, MOE/Water Resources Branch

The MISA Monitoring Regulations require submission of analytical results in electronic and printed formats. The Ministry of Environment provides customized programs that allow dischargers to meet data submission requirements. A computer based training package is also provided to assist the user in learning the use of the systems. The Data Entry Systems described include the MIDES program, for submission of analytical results, and the TOXDATA program for submission of toxicity analyses. Ministry data management systems for acceptance, storage and retrieval are briefly described.

C) Petroleum Sector Data Management Development

Dave Chapman, CCIW/Wastewater Technology Centre

Efforts under the MISA program to monitor trace contaminants in industrial and municipal effluents require systematic, clear, and consistent procedures for managing, reporting and presenting the resulting data. This presentation describes a joint project by the Ontario Petroleum Association and the Wastewater Technology Centre to develop and manage a comprehensive database containing the MISA monitoring data from the seven petroleum refineries in Ontario. The petroleum refineries will be provided with brief reports summarizing the data and comparing treatment performance on an industry-wide basis. The objectives and methodology of the project and some preliminary results will be presented.

D) MISA Organic Characterization Data Management (MOCHA) Recap

Steve Davies, MOE/Laboratory Services Branch

The MOCHA system has been developed to facilitate the reporting of MISA data from industry to MOE, in a fashion similar to MIDES. The MOCHA system has been designed specifically to allow reporting of organic characterization data, as opposed to target compound data.

(The details of this system, due to its very specific nature, will be presented in Session One - organic discussion group. At this time a recap/summary will be given for the interest of the larger group).

SESSION THREE ooo QUALITY MANAGEMENT

A) Laboratory QA/QC

Don King, MOE/Laboratory Services Branch

The MISA regulations detail specific minimum QA/QC requirements for laboratories. These will be presented along with the more general practices expected of laboratories to ensure data quality assurance and documentation.

B) MOE Laboratory Inspection Program

Catherine Doehler, MOE/Laboratory Services Branch

Laboratory inspections are an integral part of the MISA Laboratory Performance Management Plan. Components of an inspection and procedures followed during an inspection will be detailed.

Frequently encountered areas of concern will be summarized to assist laboratory staff in preparing for future inspections.

C) Petroleum Association Intercomparison Review

Allan Maynard, ASL Analytical Service Laboratories Ltd.

Prior to the implementation of the MISA regulation, the petroleum industry through Petroleum Association for Conservation of the Canadian Environment (PACE) undertook a series of studies pertaining to characterization of refinery wastewaters with respect to environmental contaminants. A significant component of these programs was directed towards developing an understanding of results variability associated with the analytical procedures.

Because of concern for analytical variability, PACE working with Ontario Petroleum Association (OPA), has undertaken two studies to investigate agreement among laboratories: One on conventional parameters; the second on volatile organics. This paper summarizes the result of these two studies.

D) MOE Round Robin Program

Sylvia Cussion, MOE/Laboratory Services Branch

An overview of the Laboratory Services Branch Round Robin Program for interlaboratory studies will be presented, including the design of each study, data review and report format. Results from several studies will be reviewed from the perspectives of problem identification and method validation.
In addition, the proposed schedule for 1990 studies will be presented.

SECTION TWO

SESSION ONE - ANALYTICAL METHODS

CHAIRPERSON: MR. JIM GREENSHIELDS, OPA

REGULATORY OVERVIEW	-	W. MOSS, MOE
METHODS COORDINATOR	-	C. RAPOSO, MOE
NIMMP	-	P. CAMPBELL, MOE
MDL PROTOCOL	-	D. KING, MOE

Minimum Sampling Requirements For MISA

MINIMUM SAMPLING REQUIREMENTS FOR MISA

- SAMPLING TECHNIQUES
- SCHEDULE 2 - SAMPLING PRINCIPLES

SAMPLING TECHNIQUE SPECIFIED FOR EACH EFFLUENT STREAM TYPE

- PROCESS EFFLUENTS
- ONCE THROUGH COOLING WATER
- STORM WATER
- EMERGENCY OVERFLOW
- LANDFARM/LANDFILL LEACHATE

PROCESS EFFLUENT SAMPLING

1. VARIABLE FLOW RATE
2. RELATIVELY STEADY FLOW RATE

DEFINITION: VARIABLE FLOW RATE

A flow rate within a day which exceeds plus or minus 15% of the daily mean flow more than 10% of the days of the year.

SAMPLING OF PROCESS EFFLUENTS WITH VARIABLE FLOW RATES

i) Automatic flow proportional refrigerated composite sampler (volume or time varying)

ii) Minimum of 8 grab samples collected at 8 times evenly spaced over the 24 hour day and combined in proportion to flow

(Applies to all chemical parameters except volatiles and sulphide)

SAMPLING OF PROCESS EFFLUENTS WITH RELATIVELY STABLE FLOW RATES

i) Automatic equal time equal volume refrigerated composite sampler (time intervals not to exceed 15 minutes)

ii) Minimum of 8 grab samples collected at 8 times over the 24 hour day and combined in equal volumes

(Applies to all chemical parameters except volatiles and sulphide)

SPECIAL REQUIREMENTS FOR CYANIDE AND PHENOLICS (4AAP)

- SAMPLES MUST BE COLLECTED IN SEPARATE CONTAINER
- PRESERVATIVES ARE ADDED PRIOR TO SAMPLING

SAMPLING OF ALL PROCESS EFFLUENTS FOR SULPHIDE AND VOLATILES

- MINIMUM OF 3 GRAB SAMPLES
- COLLECTED AT INTERVALS OF AT LEAST 6 HOURS OVER A 24 HOUR PERIOD
- AND COMBINED IN THE LABORATORY

SAMPLING FOR OIL AND GREASE

i) Automatic refrigerated composite sampling into a separate container

flow proportional or equal time equal volume as required for other chemicals

ii) Minimum of 3 grab samples

collected at intervals of at least 6 hours over the 24 hour period

and combined in the laboratory

Sampling Of Once Through Cooling Water

SAMPLING OF ONCE THROUGH COOLING WATER

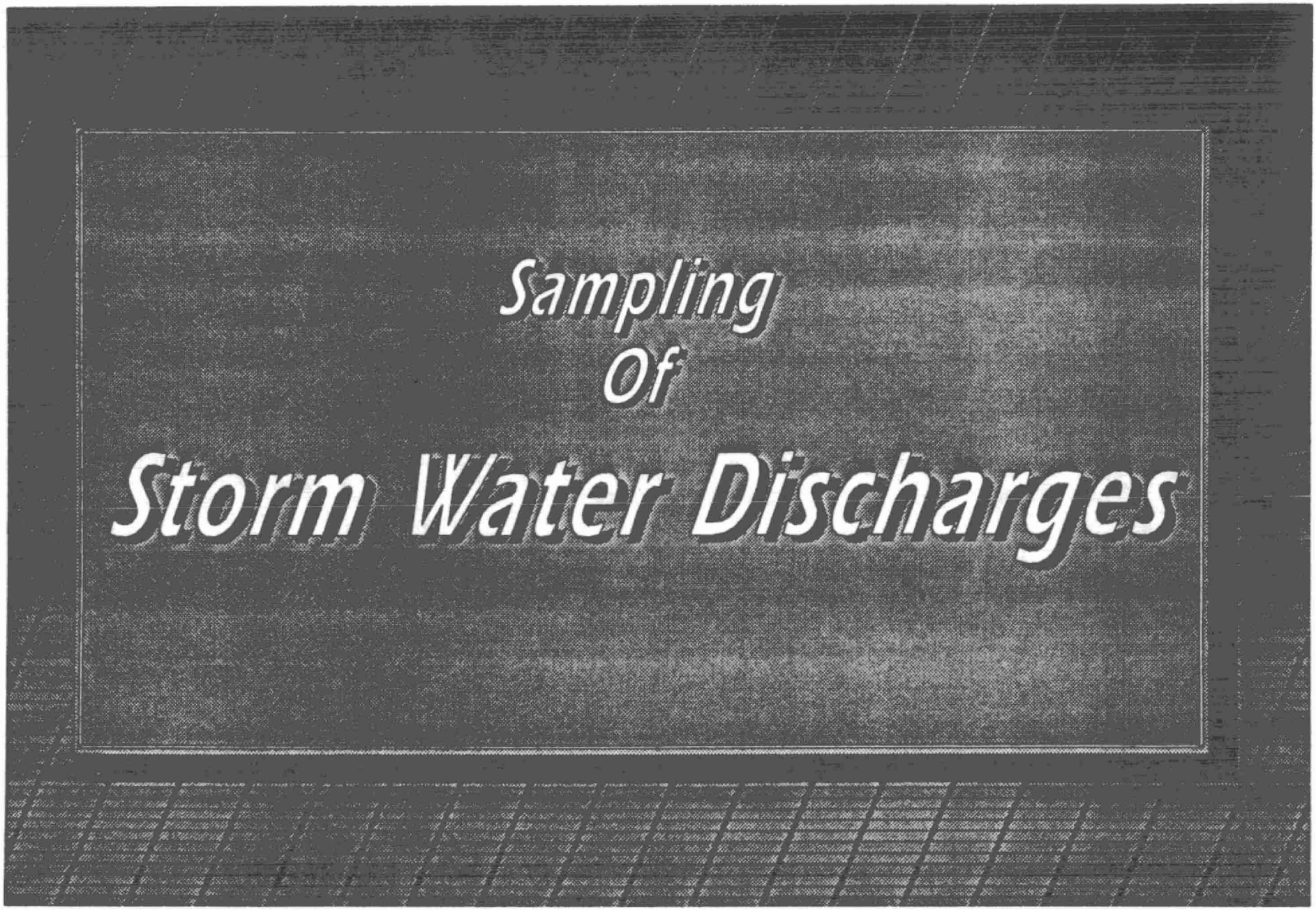
i) Minimum of 3 grab samples

collected at intervals of at least 6 hours over a 24 hour period

and combined

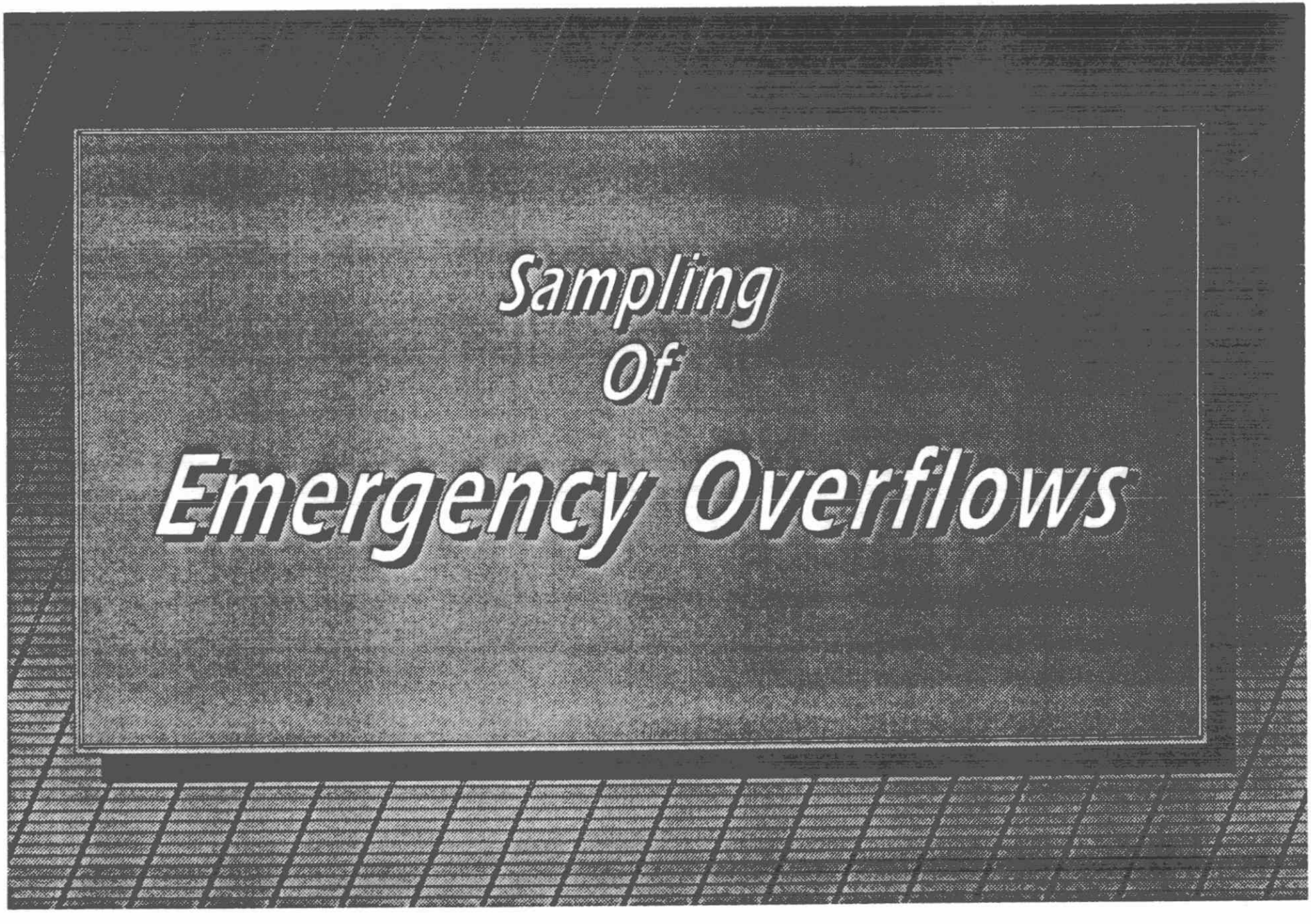
ii) Sampling as specified for process effluents

either for variable or relatively stable flow is also acceptable


Sampling
Of
Storm Water Discharges

SAMPLING OF STORM WATER DISCHARGES

A minimum of one grab sample is required for each chemical parameter specified collected near the beginning of the discharge


Sampling
Of
Emergency Overflows

SAMPLING OF EMERGENCY OVERFLOWS

A minimum of one grab sample is required for each chemical parameter specified collected near the beginning of the discharge


Sampling
Of
Collected
Landfarm / Landfill
Leachates

Schedule 2
Sampling Principles

SCHEDULE 2 - SAMPLING PRINCIPLES

THE FOLLOWING ARE SPECIFIED FOR EACH ANALYTICAL TEST GROUP:

- SAMPLE CONTAINER
- CONTAINER PRE-TREATMENT
- TEST SPECIFIC SAMPLING PRECAUTIONS
- MINIMUM SAMPLE VOLUME
- PRESERVATION METHOD
- MAXIMUM STORAGE TIME

SCHEDULE 2
Sampling Principles

Column 1	Column 2	Column 3
ANALYTICAL TEST GROUP	LABORATORY SAMPLE CONTAINER	LABORATORY CONTAINER PRE-TREATMENT
Volitiles, 16	Halogenated Sample containers and caps/liners in contact with the sample to be analyzed must be composed of only one or more of the following materials: fluorocarbon resin, glass, metallic foil	If pre-treatment is necessary: Bottle: sequence of extensive washing/hot water detergent, water, distilled water. Bake at 300°C for 8 h minimum. Cap: no pre-treatment.

SCHEDULE 2
Sampling Principles

Column 4	Column 5	Column 6	Column 7
TEST SPECIFIC SAMPLING PRECAUTIONS	MINIMUM SAMPLE VOLUME	PRESERVATION METHOD	MAXIMUM STORAGE TIME (DAYS)
If sample is high (5%) in hydrocarbons or organic solvents, use glass or fluorocarbon resin sample container only	25 mL	I) None II) Add sulphuric acid after sampling to lower pH to 2 but not 1.5	I) 4 II) 28


ANALYTICAL
REQUIREMENTS
FOR MISA

ANALYTICAL REQUIREMENTS

- Analytical Requirements
  General Regulation Text
- Analytical Principles & Analytical Method Detection Limits
  Schedule 3 in the General Regulation

ANALYTICAL REQUIREMENTS
Characterization

Sample analyses interpreted according to 2 July 1989 MOE publications

i) Techniques for the Gas Chromatography - Mass Spectrometry Identification of Organic Compounds in Effluents

ii) Guidance Document for the Elemental Characterization of Liquid Waste Samples

SAMPLING & ANALYTICAL PROTOCOLS

- Principles and protocols are specified as opposed to detailed methods
- Based on most current, recognized and accepted methods for trace environmental analysis (Ministry of the Environment, Environment Canada, USEPA)
- Facility for co-operative development of new or improved methods through joint writing groups

ANALYTICAL REQUIREMENTS
General Regulation Text

- General requirements applicable to all analytical methods (4.(1))
- Specific requirements for each analytical test group/parameter (4.(2))

ANALYTICAL REQUIREMENTS
General Regulation Text

Calibration Of Analytical Measurement Systems

- Use of standard reference materials
- Establish calibration curve for typical sample concentration
- Control charting

ANALYTICAL REQUIREMENTS
General Regulation Text

Analytical Quality Control Samples

- 4 Q.C. samples analyzed together
- Frequency of analysis:

  1 X for each group of 14 samples
  OR
  3 X for each analytical run

ANALYTICAL REQUIREMENTS
General Regulation Text

Information Obtained From Q.C. Samples

- Replicate sample - within run precision
- Method blank sample - contamination introduced in laboratory
- Spiked method blank sample - best possible recovery of each parameter
- Spiked sample - more realistic recovery of each parameter from actual samples - reflects matrix interferences

ANALYTICAL REQUIREMENTS
Impact of Method Blanks on Sample Analyses

- Method blank results must fall within established control limits

  or

- Be verified

  if not

- Corresponding samples must be reanalyzed in run with verified method blank sample

(reanalysis of samples may require resampling - except for daily samples)

ANALYTICAL REQUIREMENTS
Reporting of Sample Results

- For ATGs 1 - 15, 20 - 29:

  Report sample results corrected for positive method blank results

- For ATGs 16 - 19:

  Report sample results both corrected and uncorrected for positive method blank results

ANALYTICAL REQUIREMENTS
General Regulation Text

On-Line Analyzers

- pH, Dissolved Organic Carbon, Specific Conductance
- Must meet general & specific requirements for laboratory analytical methods
- Cross check 1 X/month with routine sampling & in laboratory analysis

ANALYTICAL REQUIREMENTS
General Regulation Schedule 3

Analytical Principles & Method Detection Limits

- Part A - Conventionals and Metals
- Part B - Organics

QUALITY CONTROL MONITORING REQUIREMENTS
General Regulation: 3(3)

- Duplicate samples
- Travelling blank samples
- Travelling spiked blank samples

QUALITY CONTROL MONITORING
Duplicate Samples

- Two samples collected at a sampling point at the same time in a manner that minimizes differences between them
- Required for every parameter/ Analytical Test Group (ATG) except open characterization (ATG. 28 & 29)

ANALYTICAL REQUIREMENTS
General Regulation Schedule 3

Analytical Principles & Method Detection Limits

- Sample preparation method principles
- Instrumental measurement method principles
- Alternate instrumental measurement method principles
- Analytical method detection limits

SCHEDULE 3, PART B - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 3	Column 4	Column 5	Column 6
SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS FOR STANDARDS IN REAGENT WATER g L
Purge and trap	Gas Chromatography Mass Spectrometry (GC MS) Capillary column	Gas Chromatography Electron Capture or Hall Single capillary column	4.3 0.6 0.8 2.8

QUALITY CONTROL MONITORING
Travelling Blank Sample

- Sample of uncontaminated water
- Travels from laboratory to sampling point with sample containers
- Open container during sampling, preserve if required, re-seal
- Returns to laboratory for analysis
- Required for every parameter/ATG except ATG 1,3,8: COD, pH TSS

QUALITY CONTROL MONITORING
Travelling Spiked Blank Sample

- Sample of uncontaminated water
- Spiked with all the compounds required to be analyzed
- Travels from laboratory to sampling point with sample containers
- Returns to laboratory for analysis
- Required for organics only: ATG 16 to 20, 23, 24, 26 and 27

QUALITY CONTROL MONITORING
Reporting

- The spiking concentrations must be reported along with travelling spiked blank sample results

QUALITY CONTROL MONITORING REQUIREMENTS

Sector Regulations

- Stream selection
- Frequency

QUALITY CONTROL MONITORING

Stream Selection

1. Process Effluent

    a. Stream with longest list of organic compounds to be monitored (monthly column of site specific schedule)

    b. Stream with longest list of all parameters to be monitored *only if no requirement for organics analysis* (monthly column of site-specific schedule)

QUALITY CONTROL MONITORING
Stream Selection

2. Combined Effluent: *Only if no process effluent*

   a. Stream with longest list of organic compounds to be monitored (monthly column of site-specific schedule)

   b. Stream with longest list of all parameters to be monitored *only if no requirement for organics analysis* (monthly column of site-specific schedule)

QUALITY CONTROL MONITORING
Stream Selection

Effluent Monitoring Regulation - Inorganic Chemical Sector Schedule:

Effluent stream:	Process				Combined				Combined			
Toxicity test required:	No				No				No			
Characterization sampling frequency (except for ATG 24):	Quarterly				Quarterly				Quarterly			
Characterization sampling minimum interval:	60 days				60 days				60 days			
Characterization frequency for ATG 24:	Semi-annually				Semi-annually				Semi-annually			
Characterization sampling minimum interval:	180 days				180 days				180 days			
Quality control monitoring required:	Yes				No				No			
Frequency of sampling:	D	TW	W	M	D	TW	W	M	D	TW	W	M

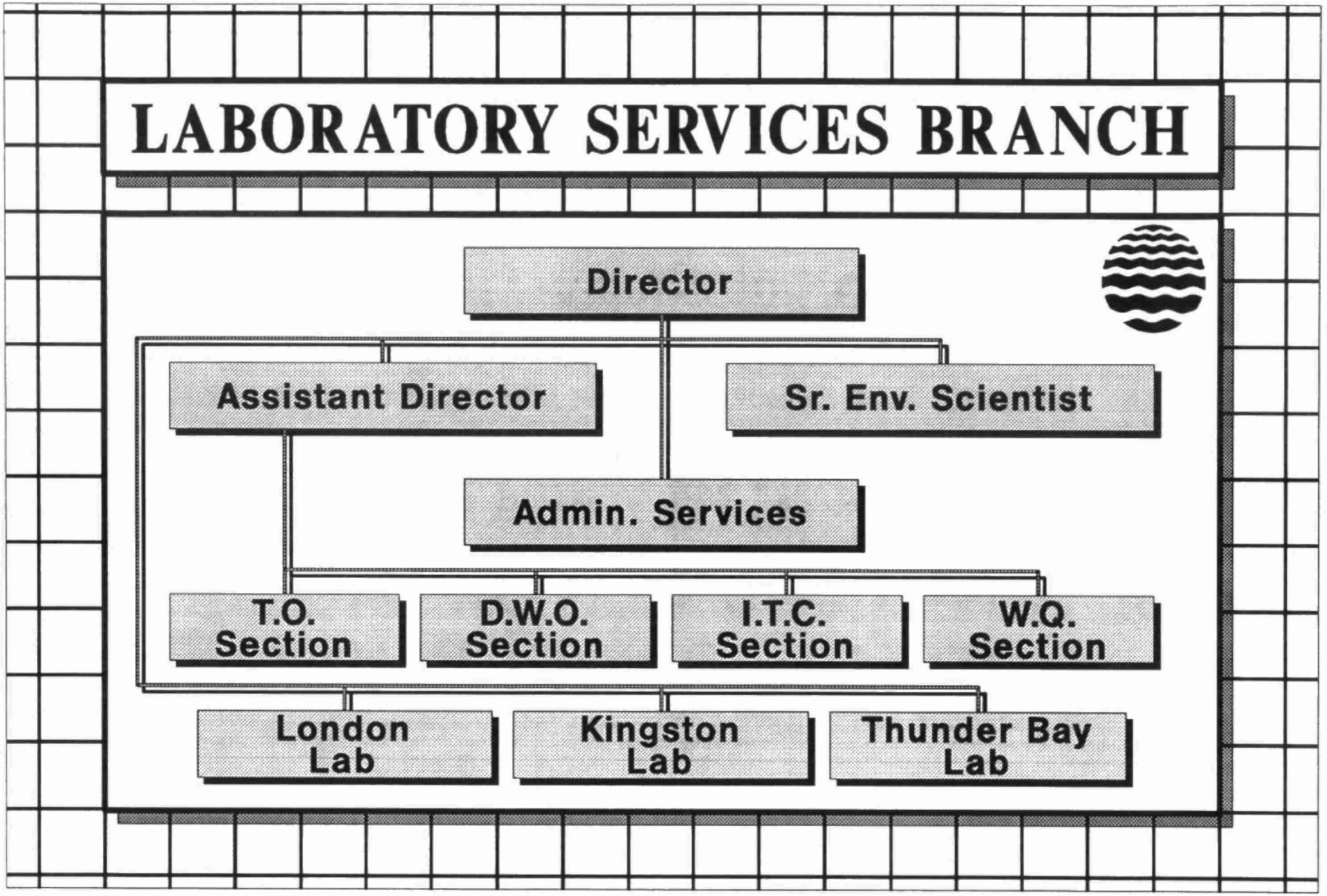
QUALITY CONTROL MONITORING

Frequency

- Once per month for parameters monitored daily and thrice weekly
- Once per quarter for parameters monitored weekly and monthly
- All 3 QC samples to be prepared/ collected on same day for all parameters
- On same day as routine samples are collected

ANALYTICAL METHOD DOCUMENTATION IN THE LABORATORY

Cammy Lynn Raposo
Quality Assurance Office
Laboratory Services Branch


LABORATORY SERVICES BRANCH
Director
Assistant Director
Sr. Env. Scientist
Admin. Services
T.O. Section
D.W.O. Section
I.T.C. Section
W.Q. Section
London Lab
Kingston Lab
Thunder Bay Lab

ANALYTICAL METHODS SUMMARY

FOR THE LSB AND REGIONAL LABS

	Total Methods	Methods Applied to MISA
TOS	26	11
DWO	25	4
ITC	96	12
WQS	93	19
London Lab*	22	-
Kingston Lab*	16	-
Thunder Bay Lab*	30	-
Total	282	35

*Not including microbiology methods

THE LSB DOCUMENTS FOUR TYPES OF ANALYTICAL METHODOLOGIES



- ◇ New methods
- ◇ Routine methods
- ◇ Methods for special / unusual needs
- ◇ Identification methods - forensic use

In most cases, methods are developed based on standard procedures (ASTM, U.S. EPA, Environment Canada, existing Environment Ontario methods)

FIVE STEPS TO METHOD DOCUMENTATION



1) Preliminary Method Investigation
   - ◇ Draft method and progress reports

2) New Method Verification
   - ◇ Run method routinely in parallel with alternative procedure
   - ◇ Document performance characteristics
   - ◇ Verify control and limit protocols

3) Routine Method Verification
   - ◇ Run method routinely; no changes
   - ◇ Inter-lab; method; analyst tests
   - ◇ QA audits
   - ◇ Final draft

FIVE STEPS TO METHOD DOCUMENTATION



4) Routine Approval
   - ◇ Fully documented
   - ◇ Reviewed / approved by Manager
   - ◇ Changes reported to QA office

5) Official Approval
   - ◇ Formal / legislative status
   - ◇ Approved by Director

ANALYTICAL METHOD FORMAT

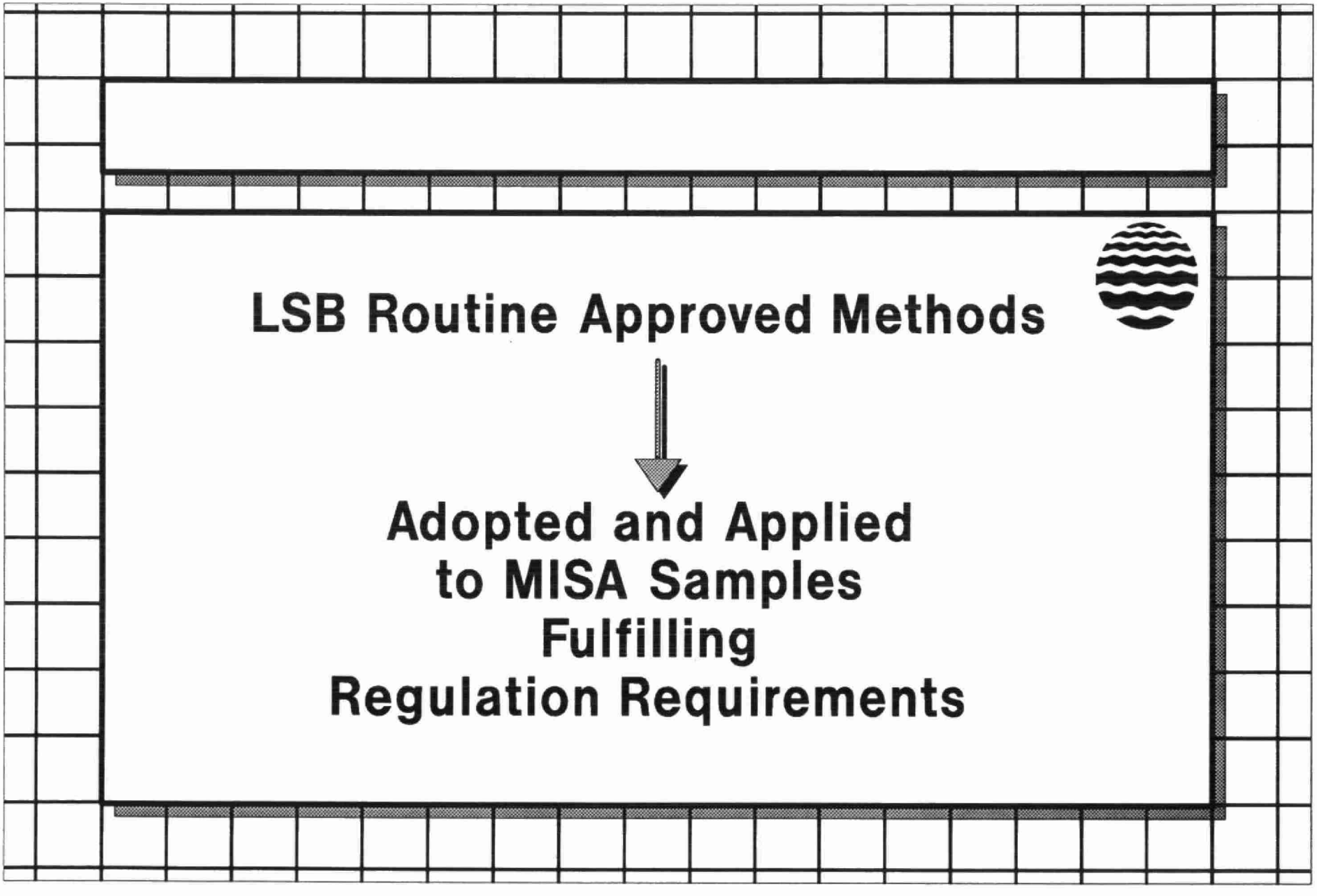


1) Summary
   - ◇ Method principle
   - ◇ Parameters measured
   - ◇ Sample matrices / requirements
   - ◇ Shortcomings / interferences
   - ◇ Analytical performance summary
   - ◇ Bibliography
   - ◇ History of changes / revisions
2) Sample Preparation
3) Analytical Processing
4) Detection System
5) Calibration / Standardization
6) Run Processing / Quality Assurance
   - ◇ Calculation / reporting
   - ◇ Detection limits
   - ◇ Proficiency testing

METHOD QUALITY ASSURANCE AUDITS



- ◇ Procedure Audits
  - Verification that test is done as outlined in written procedure
  - Direct observation
- ◇ Performance Audits
  - Evaluation of data produced by laboratory's analytical system
  - Blind audit samples/round robins
- ◇ Systems Audits
  - Assessment of laboratory's quality control system
  - On-site inspection


LSB Routine Approved Methods
Adopted and Applied
to MISA Samples
Fulfilling
Regulation Requirements

IMPORTANT ASPECTS OF THE MISA REGULATION



Schedule 3, Part A:

Principles and Analytical Method Detection Limits

Column 3 - Sample Preparation/Method Principles

Column 4 - Instrumental Measurement Method Principles

Column 5 - Alternate Instrumental Measurement Method Principles

Analytical Methods Used by Ministry Laboratories are Not Official MISA Methods

HOW TO OBTAIN ENVIRONMENT ONTARIO METHODS



- ◇ Methods Catalogue available from information table/QA Office
- ◇ Choose by catalogue code those methods specifically required
- ◇ Include name, company and address so additions can be forwarded
- ◇ One set of methods per company

WHAT'S NIMMP?

JARGON	MEANS
New	Not yet in MISA regulations
Instrumental	Equipment and Protocols
Measurement	Analysis of MISA samples
Method	Use of equipment in analysis
Principles	Fundamentals

Instrumental Measurement Method Principles (IMMP) are found in Ontario Regulation 695/89, Effluent Monitoring - General: Schedule 3A and 3B, columns 4 and 5

THE PRESENTATION



- Goal: IMMP and NIMMP
- How Did We Choose IMMP ?
- When and How Do You Add to IMMP ?
- Proposal Procedure
- Outcome
- Summary

MISA MONITORING GOAL: TO OBTAIN HIGH QUALITY DATA

Approaches for Analytical Procedures in a Regulation:



A Specify detailed methods
B Allow any method
C Provide guiding principles for rugged methods

Deciding Factors:

- **Choose "A" if you know everything about all samples**
- **Choose "B" if you don't care**
- **We chose "C" because**
  - **we didn't know everything**
  - **We care**

HIGH QUALITY DATA CAN ONLY BE ENSURED THROUGH:



SOUND QUALITY MANAGEMENT

- Quality Control (QC)
- Quality Assurance (QA)
- Good Laboratory Practice (GLP)

HOW DID WE CHOOSE IMMP ?



- **Selected From:**
  - MOE methods
  - Standard methods
  - Best professional judgement
- **Rejected When:**
  - Suspect method (e.g. not rugged, matrix)
  - Performance problems (e.g. method detection limit)
- **Missed Because:**
  - Unknown
  - Exotic
  - Unproven
  - Overlooked

WHEN AND HOW DO YOU ADD TO IMMP ?



- Start as soon as possible
- Follow procedure: - NIMMP protocol document
- Cooperate with analytical working group(s)

PROPOSAL PROCEDURE



- Brief Proposal (initial suggestion):
  - Avoid unnecessary detail
- Major Proposal:
  - Requires documents and data to assist analytical working group
- Outcomes:
  - Accepted
  - Rejected

OUTCOMES



- Accepted:
  - Adopt principles for next sector-specific regulation(s)
  - Propose for other sector(s)
- Rejected:
  - Wait one year for sector
  - Abandon or
  - Review and refine for another sector

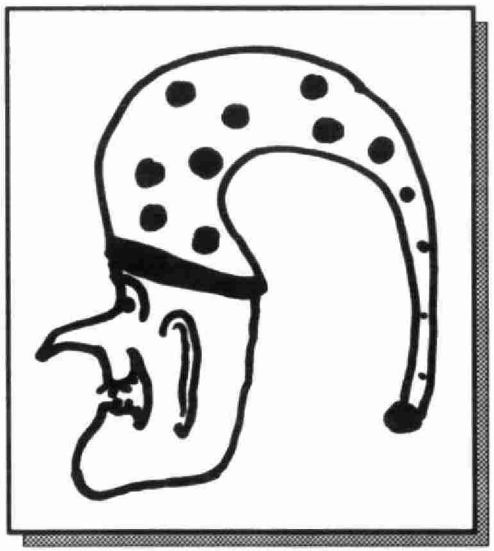
PLEASE REMEMBER

IMMP



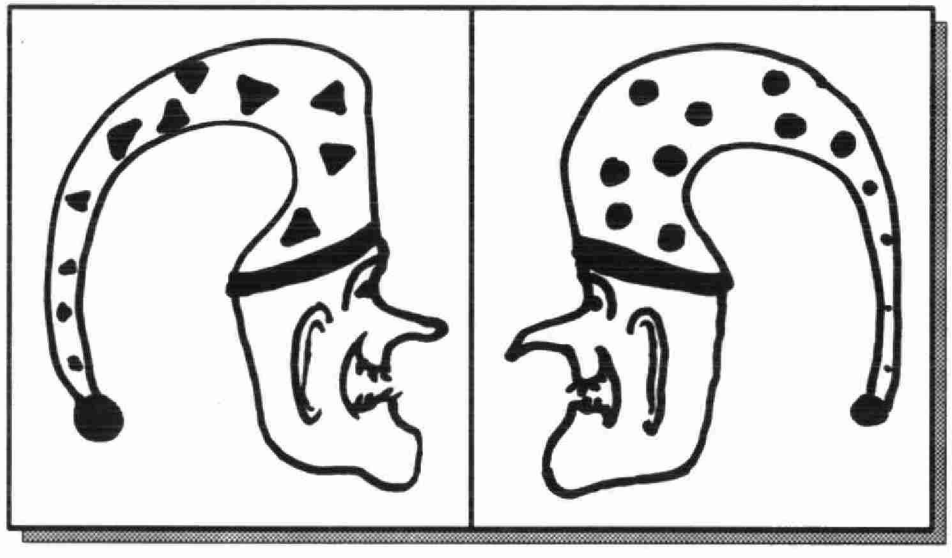
and

NIMMP



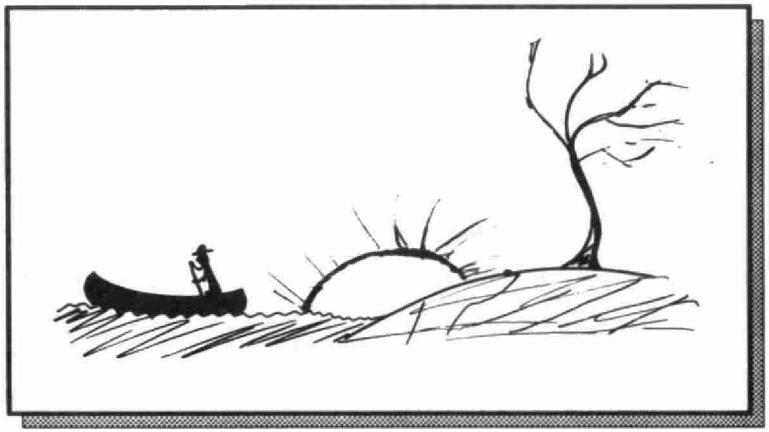
Alone
Provide No Assurance of High Quality Data

THE GOALS OF IMMP AND NIMMP:



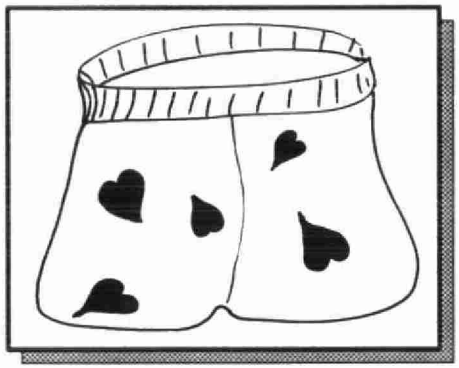
High Quality Analysis
and
Analytical Flexibility Without Chaos

THE SUMMARY



- **Goals:** High quality analysis and analytical flexibility without chaos
- **Attitude:** MOE encourages and supports new instrumental measurement method principles

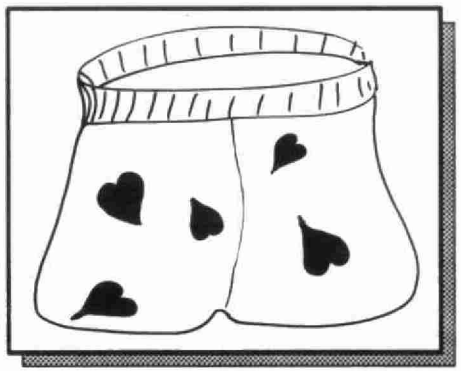
BRIEF PROPOSAL: CRITERIA FOR EVALUATION



MUST HAVE:

- Support from sector being regulated
- Principles and MDL equal or superior to regulation
- Agreement by joint working group that NIMMP are well-supported or established, and suitable for sector

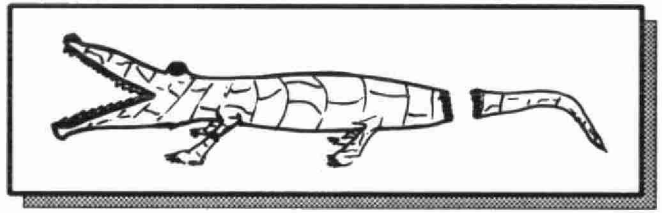
BRIEF PROPOSAL: CONTENTS



OUTLINE:

- Instrument and technology
- References and publications
- Advantages of NIMMP
- Sample preparation and analytical principles
- Known interferences
- Examples of performance (e.g. MDL obtained)

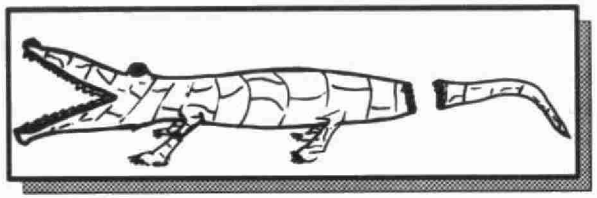
DETAILED PROPOSAL: DOCUMENTATION



BOTH IMMP AND NIMMP:

- References and publications
- Instrument specifications
- Analytical procedures
- Expected concentration range and interferences for sector
- Controls for errors and interferences
- Discussion of previous evaluation(s)

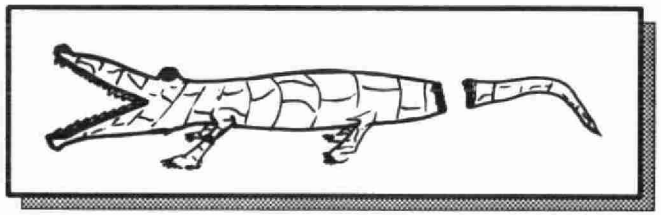
DETAILED PROPOSAL: DATA



DATA FROM USING BOTH IMMP AND NIMMP:

- Calibration graphs (8 days)
- QC charts (8 days)
- Results: - 5 representative "streams"
  - 4 samples from each
  - quadruplicate analyses
- Performance capabilities
- Interference study
- Blanks, spiked and diluted samples
- Standard reference materials if available
- Recoveries of standards if appropriate
- Other supporting data
- Data to support discussion of previous evaluations

DETAILED PROPOSAL: CRITERIA FOR EVALUATION



MUST BE:

- Complete and logical
- Consistent with good laboratory practice
- Equivalent in quality to IMMP or better
- Well executed (IMMP)

THE ANALYTICAL WORKING GROUP WILL ALSO CONSIDER:

- Relevance of references to MISA sector samples
- Statistics: distribution, curvature, bias
- Previous evaluation(s) if similar NIMMP
- Several minor problems may equal a major problem

METHOD DETECTION LIMIT CALCULATION PROTOCOLS INTERPRETATION

Donald King
Quality Assurance Office
Laboratory Services Branch

METHOD DETECTION LIMIT



- MDL & its functions
- Repeatability Sw
- Options for estimating Sw
- Formulas for Sw
- t-Factor relating Sw & MDL
- Decisions about data

METHOD DETECTION LIMIT



MDL & ITS FUNCTIONS

- A reference point
- Close to 'zero'
- Statistically defined
- Depends on repeatability Sw
- A multiple of Sw

USED FOR

- Comparison of performance
- Optional reporting limit
- Decision tool

METHOD DETECTION LIMIT



REPEATABILITY WITHIN-RUN Sw

- Instrument noise
- Method ruggedness
- Sample homogeneity
- Analyst proficiency

FACTORS NOT INCLUDED

- Calibration/stds bias
- Matrix interference
- Method under-recovery
- Mis-identification
- Chronic contamination

METHOD DETECTION LIMIT

OPTIONS FOR ESTIMATING Sw



- Low-level samples (typical) or
- Low-level spiked sample matrix
- Low-level spiked reagent water

- Eight in-run replicates, or
- Several in-run duplicates
  - collected over several days

- Separate blank for each replicate

METHOD DETECTION LIMIT

CALCULATION PROCESS



- Estimate the 'detection limit'
- Prepare/obtain samples (options)
- Perform replicate analyses
- Calculate repeatability Sw
- Determine factor t
- MDL = t . Sw

METHOD DETECTION LIMIT



SAMPLE/SPIKE CONCENTRATIONS

- Samples, or spiked samples
  - 1 to 5 times estimated MDL
- Spiked Reagent Water
  - 5 to 10 times estimated MDL
  - only option for MISA organics

METHOD DETECTION LIMIT

FORMULAS FOR CALCULATING S

For replicates: $S = \dfrac{\Sigma (X - X_i)^2}{(n - 1)}$

$S = \dfrac{n \cdot \Sigma (X_i^2) - (\Sigma X_i)^2}{n \cdot (n - 1)}$

For duplicates: $S = \dfrac{\Sigma (X_1 - X_2)^2{}_i}{2n}$

METHOD DETECTION LIMIT

EXAMPLE FOR S (REPLICATES)

$$S = \{[(n.b - a.a)/n.(n - 1)]$$

DATA	Xi - 7	$(Xi - 7)^2$
8.2	1.2	1.44
8.4	1.4	1.96
7.6	0.6	0.36
7.9	0.9	0.81
8.0	1.0	1.00
8.6	1.6	2.56
8.3	1.3	1.69
8.1	1.1	1.21
n = 8	a = 9.1	b = 11.03

$$S = \text{root } [(88.24 - 82.81)/(8 * 7)]$$

$$S = 0.311$$

METHOD DETECTION LIMIT



CALCULATED MDL

- MDL = t Sw

Sw = standard deviation within-run

t = the student's t value for n-1 degrees of freedom which predicts < 1% risk that a result > MDL would occur by chance when analyte is not present
i.e. [t(n-1), alpha = 0.01]

if n-1 = 7, t = 2.998
if n-1 > 30, t = 2.4

METHOD DETECTION LIMIT



DECISION TOOL: IS ANALYTE PRESENT ?

- **If result is ≧ MDL**
  - **analyte is present in the sample**
  - **< 1% risk of false decision**
- **If result is < MDL**
  - **analyte may be present**
  - **increased risk of poor decision**
- **MDL does not address data quality**
  - **results > MDL are not free of bias or error**

METHOD DETECTION LIMIT

QUALITY OF RESULTS BELOW MDL



- Results below MDL are precise
  - sample contains within Sw of the reported value 2/3 of the time
  - replicate sampling/analysis may confirm findings
- Results $>$ 0.25 Sw indicate presence
  - false positive decision risk $<$ 50%
- Failure to report results $<$ MDL
  - high risk of false negative decision

METHOD DETECTION LIMIT



MDL: SUMMARY OF REQUIREMENTS

- Skilled analyst
- Defined procedure
- Typical sample, or spiked reagent water
- Low-level data
- In-run replication
- Total method (blank corrected)

SECTION THREE - Data Management

SECTION THREE

SESSION TWO - DATA MANAGEMENT

CHAIRPERSON: MR. DANIEL ANDREWS, BEAK CONSULTANTS

LOW LEVEL DATA REPORTING	-	D. KING, MOE
MIDES	-	D. WEATHERBE, MOE
PETROLEUM SECTOR DATA	-	D. CHAPMAN, CCIW
MOCHA	-	S. DAVIES, MOE

LOW LEVEL DATA
- READABILITY
- REPEATABILITY
- REPORTING

Donald King
Quality Assurance Office
Laboratory Services Branch

LOW LEVEL DATA



- Data Reporting
- Data Reporting Issues
- Data Interpretation

DATA REPORTING



REQUIRED

- Test name/code
- Method code
- Units of measure
- Result
- Remark codes
- Qualifying text

DATA REPORTING

DATA QUALIFIERS (REMARK CODES)



- **INTERFERENCE CODES**
  - interference suspected — I
  - interference background — I B
  - interference colour — I C
  - interference sample matrix — I M
- **LOW-LEVEL DATA CODES AVAILABLE**
  - tentative data qualifier — < T
  - < lab MDL qualifier — < DL
  - zero qualifier — < W

DATA REPORTING

LABORATORY METHOD DETECTION LIMIT



- Ministry MDL protocol
- Lab must calculate MDL at least once and report it via industry initial report
- Lab MDL must be ≦ reg MDL
- Reg MDL's listed in Schedule 3
- Every effort must be made to measure samples down to lab MDL
- Results at or above lab MDL must be reported

LOW LEVEL DATA



- Data Reporting
- Data Reporting Issues
- Data Interpretation

DATA REPORTING ISSUES



- **SIGNIFICANT FIGURES**
  - readability
  - repeatability
- **REPORTING LIMIT**
  - low-level data
  - decision errors
- **SAMPLE SUITABILITY**
  - homogeneity
  - matrix effects
- **DATA QUALITY**

DATA REPORTING ISSUES



READABILITY

- Readings are digitized for reporting purposes
- Increments are arbitrary
  - instrument readout
  - operating range
- Rounding off
  - repeatability
  - significant figures
- Non-measurable results
  - "zero" measurements
  - how low could you read
  - < W: not measurable

LOW LEVEL DATA

REPEATABILITY (Sw)



- Sw: Within-run Standard Deviation
  - method, skill, sample
  - determines the significance of a small change in reading
- Reliable Estimates of Sw
  - reading increment < Sw
  - adequate data (8 replicates)
- Report Sw to Two Figures
  - used to compare performance
  - defines significant figures

DATA REPORTING ISSUES



REPORTABILITY

- A response is seen, identified, measured, and evaluated
- Low measurements should be qualified (< T option)
- Low measurements below lab MDL should be qualified (< DL option)
- Should low data be reported?

A REPORTING ISSUES

ASSURING REPORTABILITY



- Analytical Concerns
  - correct calibration
  - blank correction
  - analyte identification
  - matrix effects
  - possible data misuse
- Tools
  - quality control checks
  - sample/method suitability
  - document analytical problems
  - use data qualifiers
  - consult data users re needs

LOW LEVEL DATA



- Data Reporting
- Data Reporting Issues
- Data Interpretation

DATA INTERPRETATION



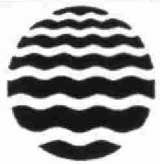
- **Data Users Concerns**

  - possible bias
  - actual presence/absence
  - public reaction

- **Tools**

  - frequency of occurrence
  - observed trends/outliers
  - magnitude/distribution
  - statistical evaluation
  - associated field data
  - analyst concerns

DATA INTERPRETATION



DECISION ERRORS

- **False Positive Decisions**
  - take unnecessary action
  - low-level values may be biased, mis-identified
- **False Negative Decisions**
  - fail to take necessary action
  - low-level values are repeatable
  - < values misinterpreted as "zero"
- **LSB Low-Level Data Policy**
  - low-level data is reportable
  - measurements must be controlled
  - results must be qualified

DATA INTERPRETATION



REPORTABILITY

- A Response Is Seen, Identified, Measured, and Evaluated

Should Low-Level Data Be Reported ?

- Low-Level Data May Distinguish Among Trace Analytes:
  - never detected
  - occasionally detected
  - always detected

DATA REPORTING SUMMARY



- Many organics and metals are at or below current "Batea" method MDL's
- Measurements can be made below 1/5 MDL
- Low-level data is prone to under-recovery and censoring
- High risk of false negative decisions
- Ministry needs low-level data to validate results at or above LMDL

MISA DATA ENTRY PROGRAMS

By Don Weatherbe
Water Resources Branch

Abstract

The MISA Monitoring Regulations require submission of analytical results in electronic and printed formats. The Ministry of Environment provides customized programs that allows dischargers to meet data submission requirements. A computer based training package is also provided to assist the user in learning to use the systems. The Data Entry Systems described include the MIDES program, for submission of analytical results,and the TOXDATA program for submission of toxicity analyses. Ministry data management systems for acceptance, storage and retrieval are briefly described.

List of Overheads Used in Presentation

1. MISA Monitoring - Data Reporting Requirements
2. General Regulation - Reporting Requirement
3. Data Entry Route
4. Data Entry Route Continued
5. MISA Monitoring Data Submission Format
6. Typical Industrial Plant Site Monitoring Locations
   Note: All types of locations accommodated by data entry systems.
7. MIDES - Programme Considerations
8. Mides - Programme Diskettes
9. Sample Collection Information
10. Analytical Results Information
11. MIDES - Main Menu Structure
12. MIDES - Installation Menu
13. MIDES - Update Method Detection Limit Menu
14. MIDES - Add Sample Data Menu
15. MIDES - Add Sample Data Screen
16. MIDES - Data Entry Fields

17. General Regulation - Requirement for Submission of Data Below Detection Limit

18. MIDES - LIST Report Sample

19. MIDES - Report for Transmittal Sample

20. MIDES - Transmittal Sheet

21. MISA Industrial Data Flow - Discharger's View

22. Computer Based Training (CBT) for MIDES and TOXDATA

23. MIDES CBT - Training Units

24. MIDES CBT - Sample Questions and Answers

25. MISA Data Systems - Ministry to Industry Hand Off

26. MISA Data Systems Users Guide - Title Page

27. Distribution and Support of Data Systems

28. MIDES and TOXDATA - Licence Agreement (Part)

OVERHEAD #1

MISA MONITORING

Data Reporting Requirements

Submission of analytical results, including chemistry and toxicity data

Analytical results must be submitted to the Regional Director, care of local Ministry District Office

Both written and electronic forms of the data must be submitted

OVERHEAD #2

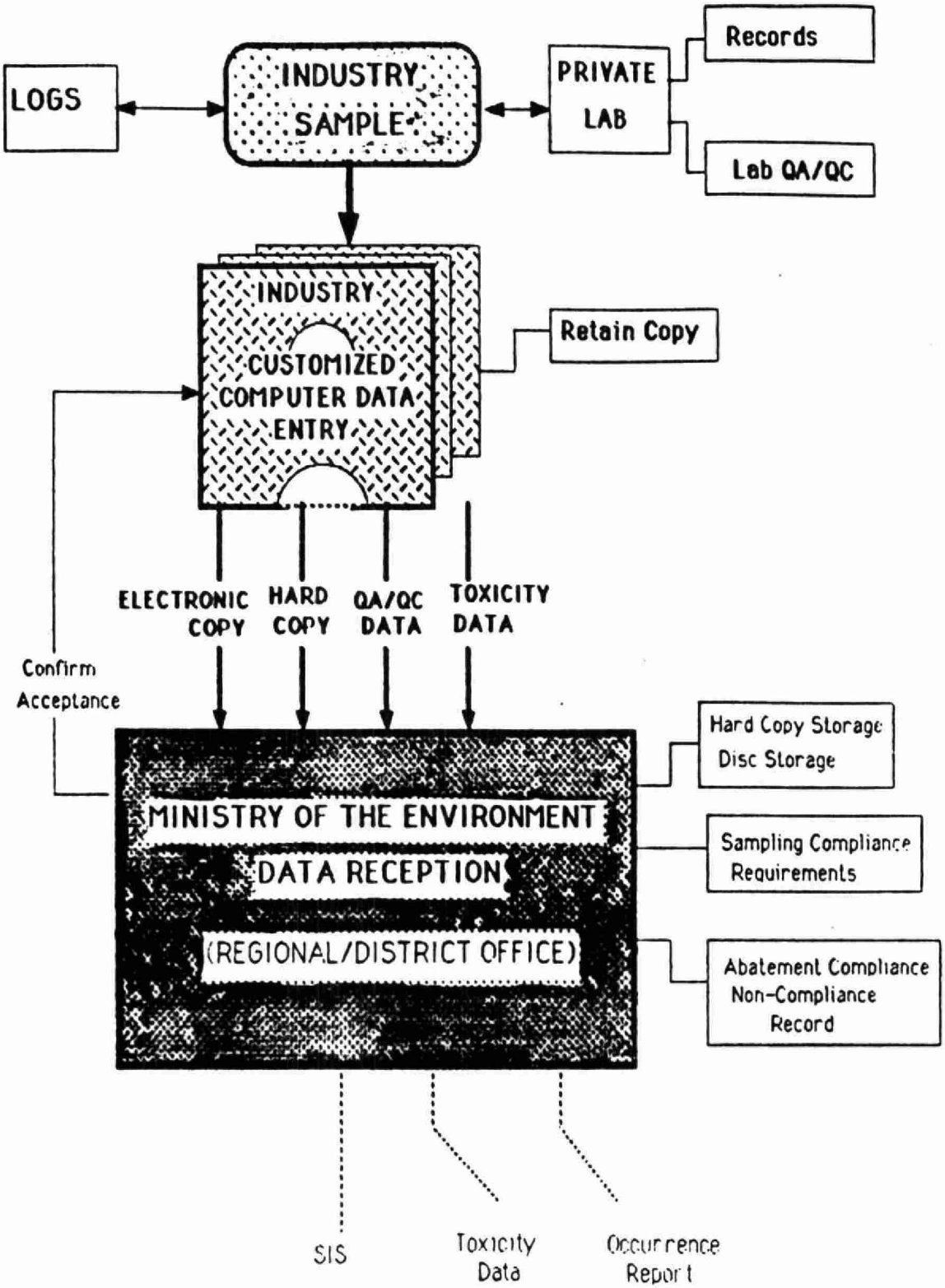
7. (2) EVERY DIRECT DISCHARGER SHALL REPORT THE RESULTS OF ALL ANALYSES OF SAMPLES THAT ARE REQUIRED TO BE REPORTED TO THE DIRECTOR BY A SECTORAL EFFLUENT MONITORING REGULATION, ON A FLOPPY DISKETTE IN A FORMAT ACCEPTABLE TO THE DIRECTOR AND BY HARD COPY GENERATED FROM THAT DISKETTE AND SIGNED BY THE DISCHARGER,

(A) WITHIN SIXTY DAYS AFTER THE DAY ON WHICH SAMPLES WERE COLLECTED, EXCEPT FOR RESULTS OF CHRACTERIZATION' OPEN CHRACTERIZATION AND ANALYSIS FOR PARAMETERS IN ANALYTICAL TEST GROUP 24 IN SCHEDULE 1; AND

(B) WITHIN NINETY DAYS AFTER THE DAY ON WHICH THE SAMPLE WAS COLLECTED, FOR RESULTS OF CHARCTERIZATION, OPEN CHARACTERIZATION AND ANALYSES OF THE PARAMETERS IN ANALYTICAL TEST GROUP 24 IN SCHEDULE 1.

MISA DATA MANAGEMENT STRATEGY

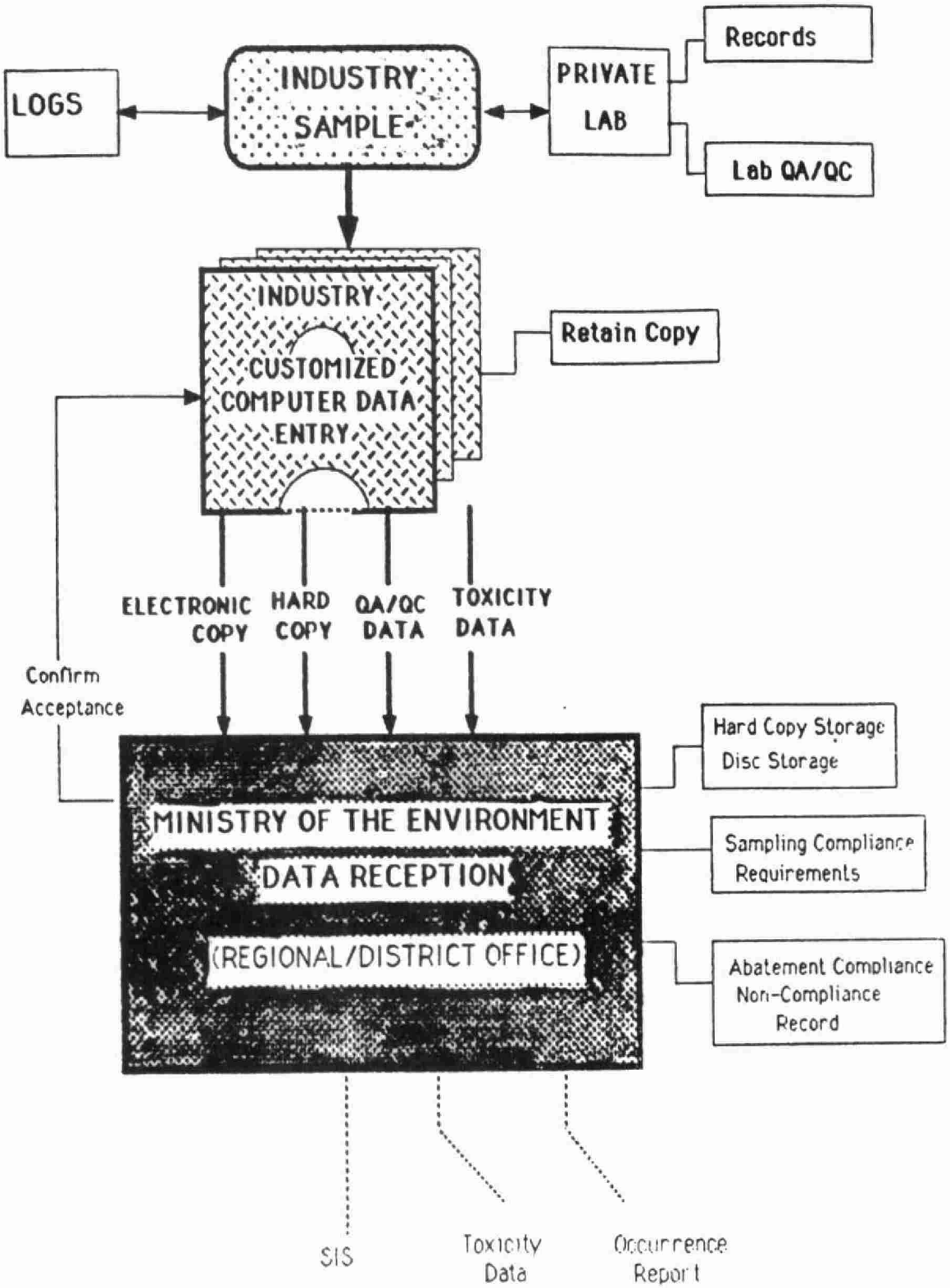
DATA ENTRY ROUTE



OVERHEAD #3

MISA DATA MANAGEMENT STRATEGY

DATA ENTRY ROUTE



OVERHEAD #4

OVERHEAD #5

MISA MONITORING

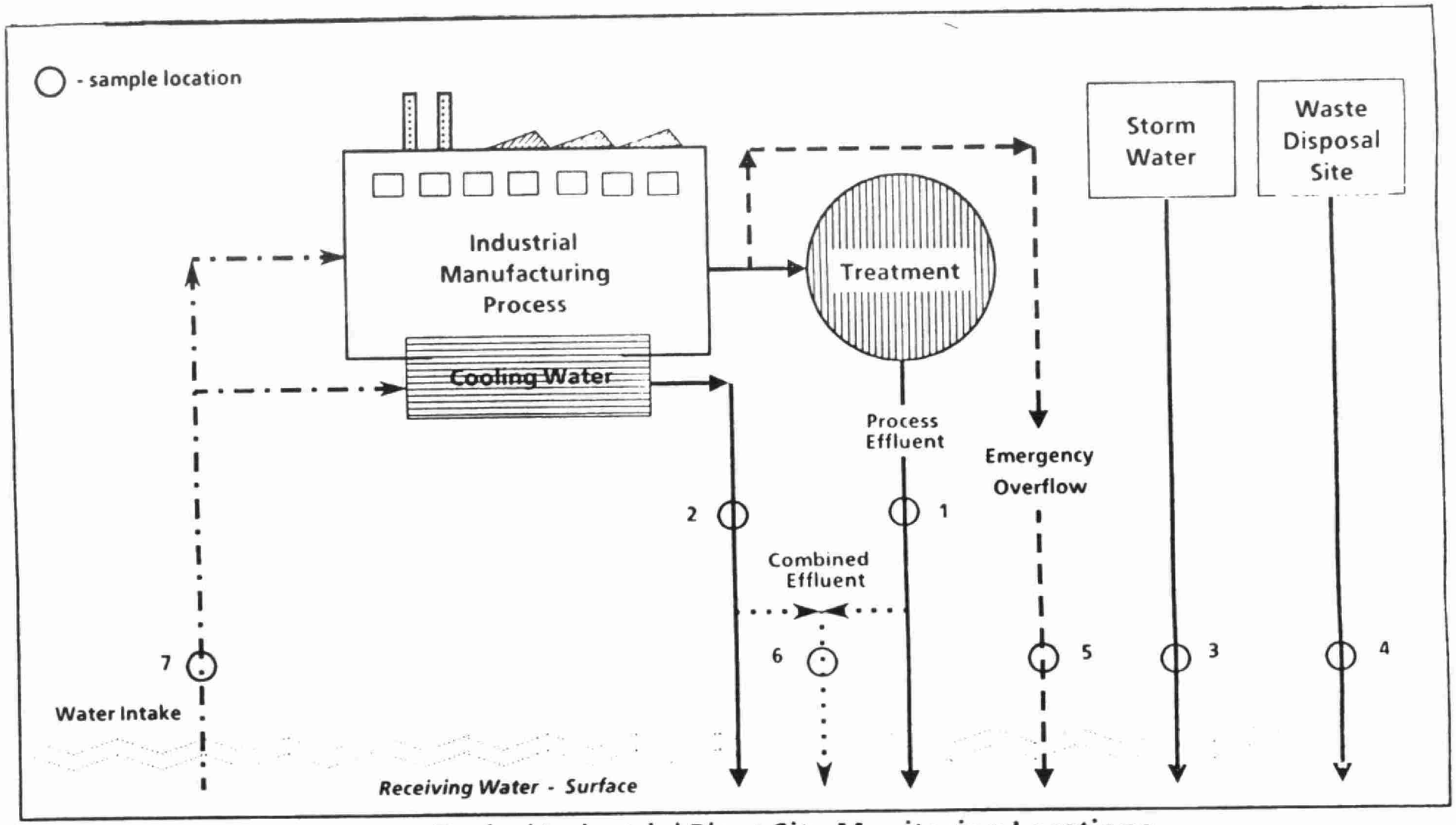
Data Submission Format

- Electronic Transfer File (ETF)

- Hardcopy

- Both formats are generated by MISA Data Systems

OVERHEAD #6



Typical Industrial Plant Site Monitoring Locations

MIDES

Programme Considerations

Stream Types

- process effluent
- OTCW
- combined effluent
- batch discharge
- stormwater
- waste disposal site effluent
- emergency overflows

Sampling Locations

- discharge outlets
- rain gauges

Frequencies

- daily
- thrice weekly
- weekly
- monthly
- annually
- discharge events

(Other frequencies to be accommodated at later date)

Other

- non-MISA data

OVERHEAD #7

OVERHEAD #8

MIDES

Programme Diskettes

Each company will receive customized MIDES diskettes

Ministry customizes each MIDES diskette

- company name and ID #
- company location/mailing address
- sampling location information:
  - stream type (control point)
  - ID #
  - parameters to be sampled
  - frequency of parameters to be sampled

OVERHEAD #9

MIDES

Sample Collection Information

- sample collection agency identification
- sample collection date and time (time - optional)
- sample ID #
- collection method
- designation as QA/QC, if applicable
- remarks (code)

OVERHEAD #10

MIDES

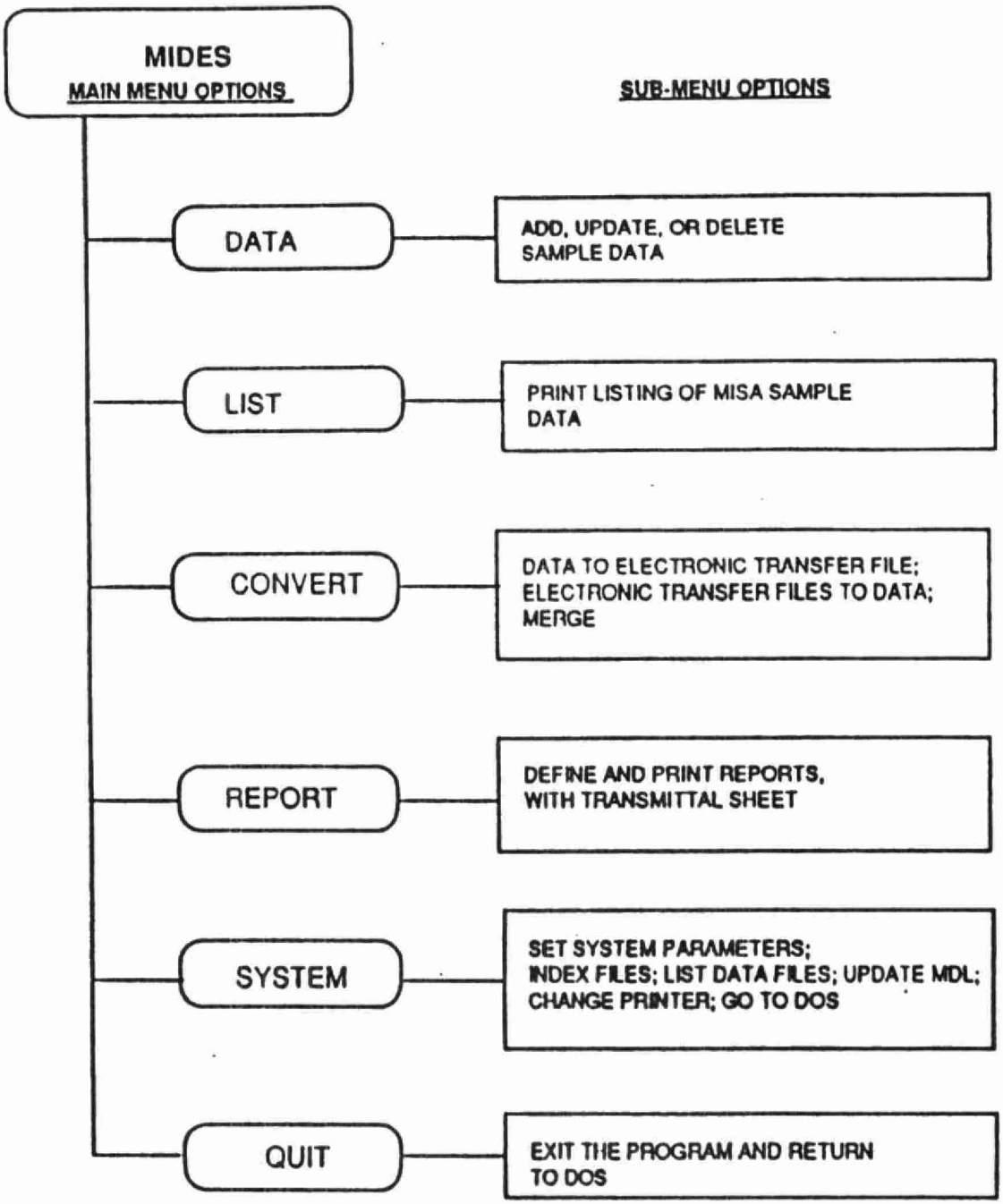
Analytical Results Information

- analyzing agency identification
- date analysis performed
- analytical method used *
- analytical method detection limit (MDL) *
- numerical result
- remarks

* *MAINTAINED BY DISCHARGER*

OVERHEAD #11

MIDES System Menu Structure



OVERHEAD #12

5.3 Installing the MIDES System

The following screen appears:

Figure 7

```
INSTALLATION PROGRAM - HARD DISK VERSION
SYSTEMS INFORMATION AND TECHNOLOGY BRANCH - MINISTRY OF THE ENVIRONMENT

   Enter the letter for the FLOPPY drive
     which contains this DISTRIBUTION diskette ..... [ A ]
   Enter the drive letter for your HARD disk ..... [ C ]
   Enter the name of the directory where the
     program should be installed. If it does not exist,
    I will create it ..... [\MIDES5          ]

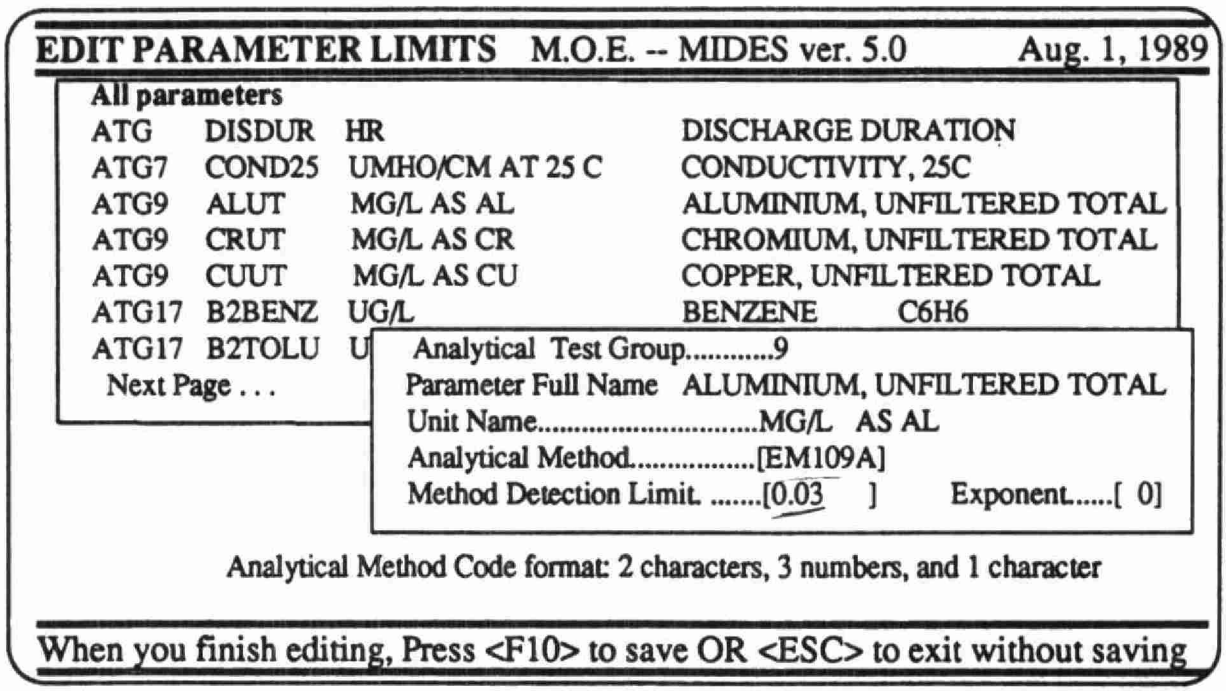
   Enter the letter of the FLOPPY or HARD drive
     on which the DATA files will be entered ..... [ C ]
   Enter the name of the directory where the data
     files will be kept. If it does not exist, I will
    create it ..... [\MIDES5\DATA      ]
```

OVERHEAD #13

6.4 Initial Use of MIDES - Update MDL Table

The following screen appears:

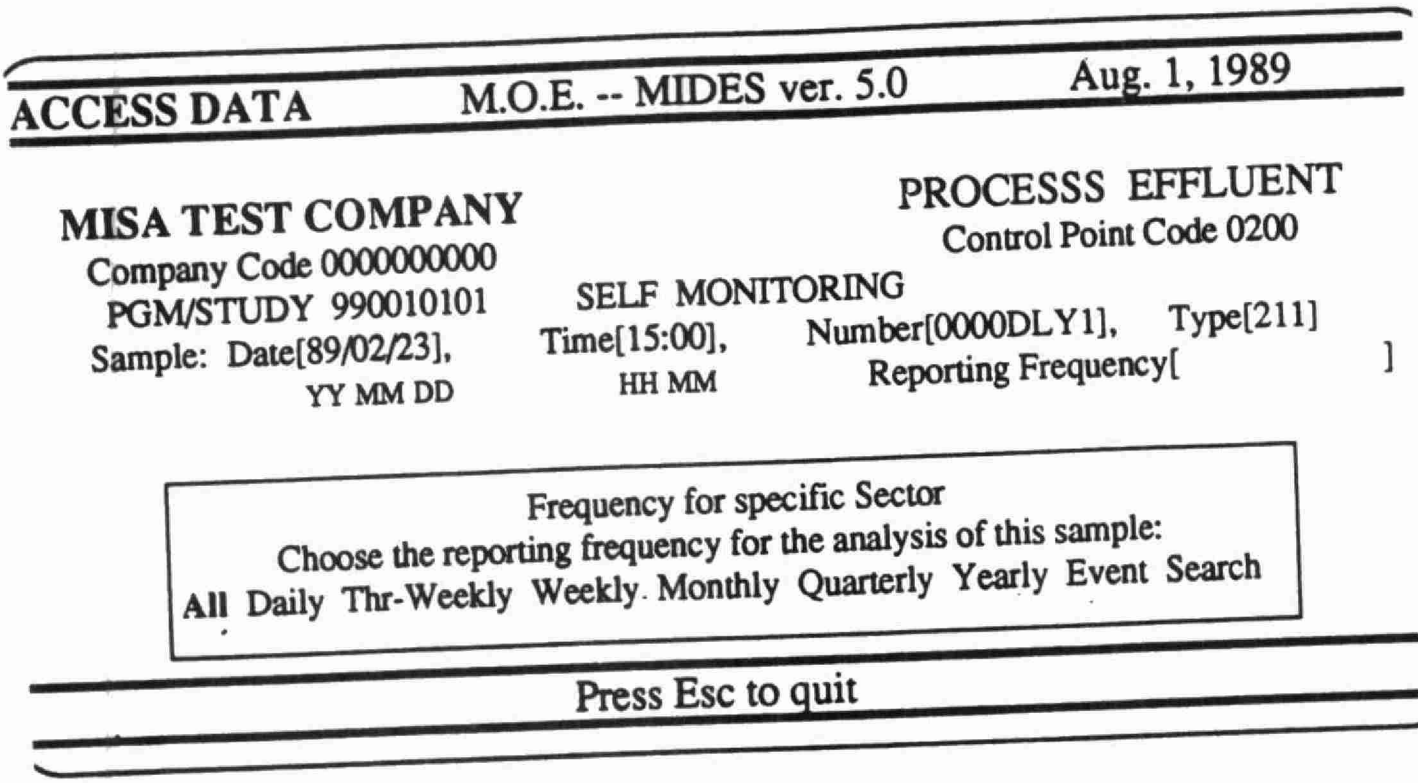
Figure 3



Use the up and down arrow keys to move from field to field.

OVERHEAD #14

Figure 3



OVERHEAD #15

ACCESS DATA M.O.E. -- MIDES ver. 4.11 Feb 23, 1989

MISA TEST COMPANY
Company Code 0000000000
PROCESSS EFFLUENT
Control Point Code 0100
PGM/STUDY 990010101 Sampling Agency 0000000000 Analyzing Agency 0000000000

Sample: Date[89 / 02 / 23], Time[15 : 00], Number[0000DLY1], Type[211]
YY MM DD HH MM Reporting Frequency[DAILY]

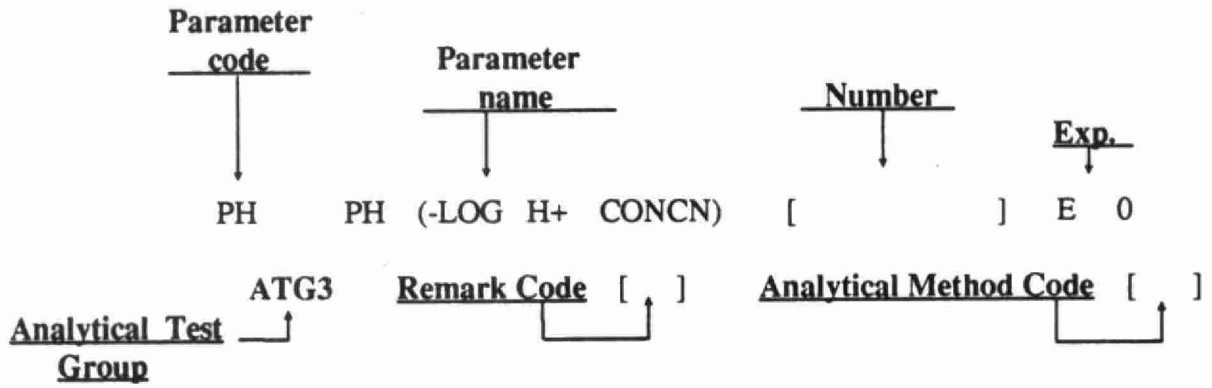
FTFLOW	FLOW	E	0	M3	/DAY
	Remark Code [ ] Analytical Method Code				
PH	PH (-LOG H+ CONCN)	E	0		
	Remark Code [ ] Analyical Method Code			MT001A	
RSPLOI	RESIDUE,PART LOSS ON IGNIT	E	0	MG /L	
	Remark Code [ ] Analytical Method Code			MT025B	
PHNOL	PHENOLICS, UNFILTERED REACTIVE	E	0	UG/L	PHENOL
	Remark Code [ ] Analytical Method Code			MT035A	

F4: no discharge F5: data not detected F6: no data F7: done

OVERHEAD #16

7.1 To Add sample data using the DATA option

7.1.4 New Data Entry



Data ID Fields

Parameter Code - Displays the unique descriptor code assigned to each parameter. This code is up to 6 characters long and is not accessible to the user.

Parameter Name - Displays the full name of the parameter. Up to 29 characters can be displayed. In a few cases the name is abbreviated to fit the space. This field is not available to the user.

Analytical Test Group - displays the analytical test group number for each parameter as outlined in regulations schedules

OVERHEAD #17

7. (3) A DIRECT DISCHARGER MAY REPORT ANALYTICAL RESULTS THAT FALL BELOW THE ANALYTICAL METHOD DETECTION LIMITS CALCULATED IN ACCORDANCE WITH SUBSECTION 4(3A) BY THE LABORATORY PERFORMING THE ANALYSIS EITHER AS THE ACTUAL RESULT OR AS THE CALCULATED MDL PREFIXED BY THE SYMBOL " ", SUPPORTED BY THE THE REMARK CODE " DL".

OVERHEAD #18

August 22, 1989 Ontario Ministry of the Environment Page 1
Municipal & Industrial Strategy for Abatement

MISA TEST COMPANY - PROCESS EFFLUENT
Company Code: 0000000000 Control Point Code: 0200
PRG/Study: 990010101 MISA Self-monitoring

Date: 89/06/01 Sample No.: UNCOR001 Type: AAU Freq: Monthly

ATG	Param. Code	Parameter		Value	Exp	Unit	Rem	Anal. Method
16	XIBMET	BROMOMETHANE		5.0E	0	UG/L		EM116A
16	X1CHLO	CHLOROFORM CHCL3		0.7E	0	UG/L		EM116A
16	X2CBEN	CHLOROBENZENE		1.0E	0	UG/L		EM116A
17	B2BENZ	BENZENE	C6H6	1.5E	0	UG/L		EM117A
17	B2TOLU	TOLUENE	C7H8	1.0E	0	UG/L		EM117A
19	PMCAMP	CAMPHENE		3.5E	0	UG/L		EM119A
19	PNPYR	PYRENE		0.8E	0	UG/L		EM119A

Date: 89/06/01 Time: 14:00 Sample No.: 0000XYZ1 Type: 201 Freq: Monthly

ATG	Param. Code	Parameter		Value	Exp	Unit	Rem	Anal. Method
16	XIBMET	BROMOMETHANE		3.7E	0	UG/L	<DL	EM116A
16	X1CHLO	CHLOROFORM CHCL3		0.7E	0	UG/L	<DL	EM116A
16	X2CBEN	CHLOROBENZENE		0.7E	0	UG/L	<DL	EM116A
17	B2BENZ	BENZENE	C6H6	0.5E	0	UG/L	<DL	EM117A
17	B2TOLU	TOLUENE	C7H8	0.5E	0	UG/L	<DL	EM117A

THIS INFORMATION IS SUBMITTED UNDER ONTARIO REGULATIONS:
XXX/88 - Effluent Monitoring General
AND
XXX/89 -

Signature of Company Official:_____

Print Name/Title of Company Official:_____

Telephone: (___)_____ Date:_____

MOE - MIDES CONTROL POINT DETAIL REPORT REPORT DATE: Aug 22 89 10:21 PAGE: 1
COMPANY/PLANT: MISA TEST COMPANY COMPANY/PLANT CODE: 0000000000
CONTROL POINT: PROCESS EFFLUENT CONTROL POINT CODE: 0200

SAMPLE DATE YYMMDD	TIME HHMM	SAMPLE NUMBER	TYP	F	FTFLOW FLOW M3 /DAY	PH PH (-LOG H+ CONCN)	RSPLOI RESIDUE,PART LOSS ON IGNIT. MG/L		PHNOL PHENOLICS, UNFILERED UG/L	PHENOL	DOC CARBON, DISSOLVED ORGANIC MG/L	AS C
890601	1400	0000XYZ1	208	M							10.0	
890601	1400	DAILY001	208	D	10320	7.9	30	AR	5			
890601	1400	DUPL0001	FAA	D	12465	7.8	18		5.5			
890602		DAILY431	208	D	9870	7.5	15		4			
890603		DAILY094	208	D	15326	7.8	17		4.3			
890604		DAILY642	208	D	54674	7.6	16.4		3.7			
605		DAILY975	208	D	7566	7.9	24		4.6			
890606		DAILY004	208	D	9875	7.7	13		3.8			
890608		DAILY234	208	D	10235	7.7	14.6		4.1			
890609		00DAILY3	208	D	9998	7.8	16		3.1			
890610		0DAILY42	208	D	8749	7.9	21		2.9			

OVERHEAD #19

MINISTRY OF THE ENVIRONMENT
MISA TRANSMITTAL SHEET

FROM: MISA TEST COMPANY
MISA COMPANY CODE: 0000000000

COMPLETE THIS FORM AND SUBMIT WITH MIDES DISKETTE(S) AND REPORT TO :

The Director,
C/O Regional Office District Office
MINISTRY OF THE ENVIRONMENT
456 Government Grove
Regiontown, Ontario
Z9X 8Y7

SUBMISSION INCLUDES THE FOLLOWING (Use reverse if necessary) :

Number of: MIDES Diskettes _____ Report Pages _____

DISKETTE LABEL	CNTL PT CODE	SAMPLE FREQUENCY DLY	THR	WKL	MON	QRT	YRL	ALL	OTH	SAMPLING PERIOD FROM	TO
==========	======	===	===	===	===	===	===	===	===	========	========
----------	------	---	---	---	---	---	---	---	---	--------	--------
----------	------	---	---	---	---	---	---	---	---	--------	--------
----------	------	---	---	---	---	---	---	---	---	--------	--------
----------	------	---	---	---	---	---	---	---	---	--------	--------
----------	------	---	---	---	---	---	---	---	---	--------	--------
----------	------	---	---	---	---	---	---	---	---	--------	--------
----------	------	---	---	---	---	---	---	---	---	--------	--------
----------	------	---	---	---	---	---	---	---	---	--------	--------

DATA INCOMPLETE? YES / NO
IF YES, WHY? _____
_____

LATE SUBMISSION? YES / NO
IF YES, WHY? _____
_____

RE-SUBMISSION? YES / NO
IF YES, WHY? _____
_____

OTHER COMMENTS?_____

THIS INFORMATION IS SUBMITTED UNDER ONTARIO REGULATIONS:
695/88 -Effluent Monitoring General
AND
359/88 -Petroleum Sector

Signature of Company Official :_____

Print Name/Title of Company Official :_____

Telephone: (___)_____Date: _____

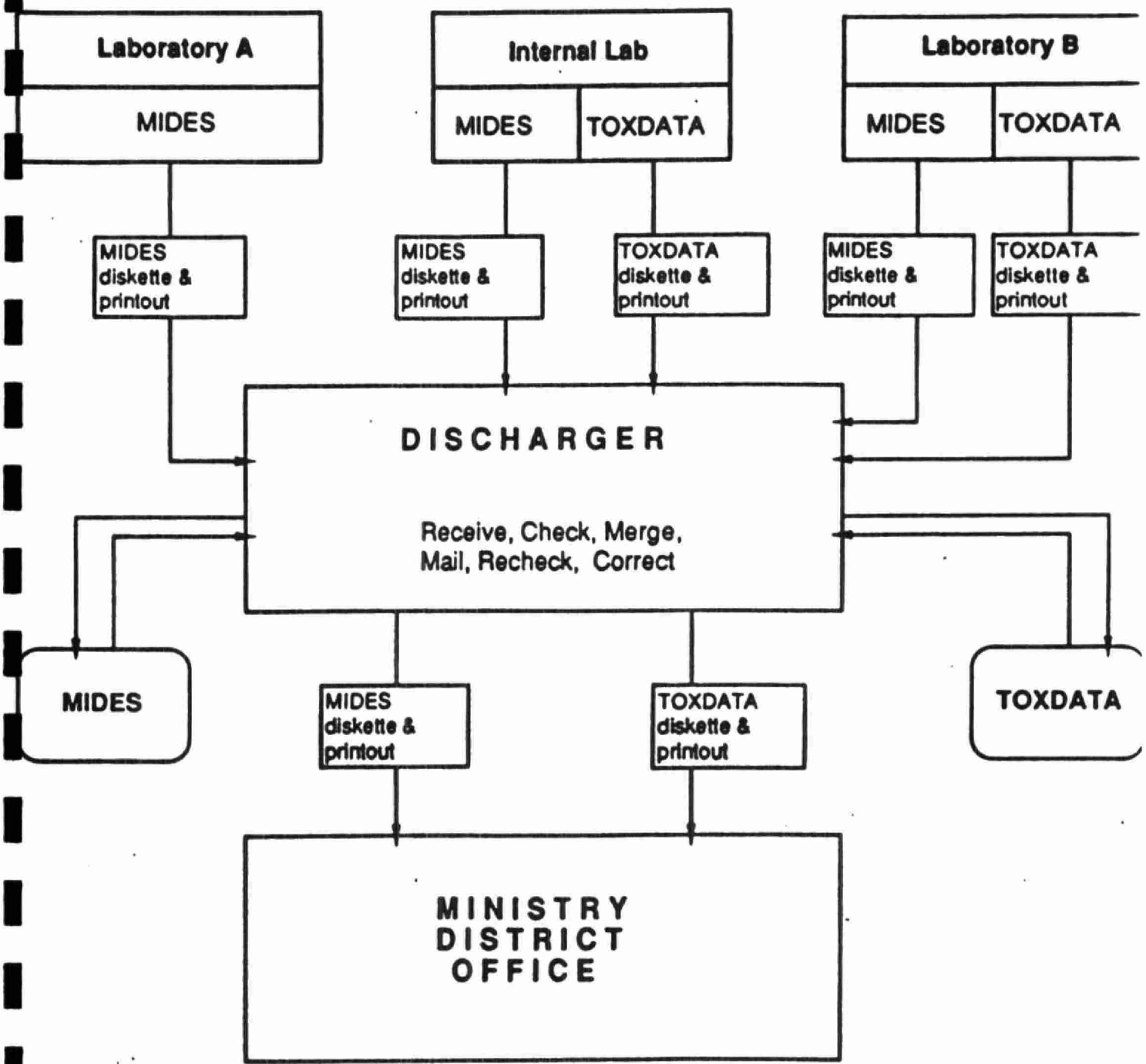
==========

MINISTRY USE ONLY
Number of Diskettes/Pages RECEIVED as specified:_____

OVERHEAD #20

OVERHEAD #21

MISA INDUSTRIAL DATAFLOW - DISCHARGER VIEW



OVERHEAD #22

COMPUTER BASED TRAINING FOR MIDES AND TOXDATA

GOAL: Information and Skill to Enter Monitoring and Toxicity Data

. A Self Teaching Tool

. Requires Knowledge of:

- DOS
- Regulatory requirements

. Hardware:

- IBM Compatible
- 640K RAM
- DOS 3.2 or higher
- Color monitor preferred
- Hard Drive with 1.4Mb. free

\+ - 5 disks supplied
\+ - Guide

OVERHEAD #23

MIDES CBT

UNITS:

- How to Move Around
- Getting Started
- Data Input and Editing
- Data Listing Function
- Data Report and Transmittal Sheet
- Data Conversion
- Questions and Answers
- The Final Word

OVERHEAD #24

~UNIT G: Questions and Answers ~System Operation~

The routine use of MIDES would involve:

Step 1 Entering sample data using the DATA function
Step 2 Check entered data using the LIST function
Step 3 Use the REPORT function to generate a Control Point Detail Report and Transmittal sheet
Step 4 Use the CONVERT function to prepare an Electronic Transfer File (ETF) for submission to the Ministry
Step 5 Label the ETF diskette in the top right corner with the MISA company code and the date of submission
Step 6 Apply a write protect sticker to the ETF diskette
Step 7 Complete the transmittal sheet
Step 8 Forward the ETF diskette, Control Point Detail Reports, Transmittal sheet, and any additional reports (i.e. references to remark codes, malfunction reports, etc.) to the appropriate Ministry Regional Office.

~<F1> options ~Press <Enter> to return to the System Operation Menu ~

OVERHEAD #25

MISA DATA SYSTEMS

Ministry to Industry Hand-off

Ministry provides customized diskettes one month prior to the start of sampling

Ministry conducts 1/2 day Hand-off Seminar

Computer-based (self) training (CBT) program distributed to Industry

MISA Data Systems User's Guide for MIDES and TOXDATA distributed to Industry

STOPPING WATER POLLUTION AT ITS SOURCE



MISA

Municipal/Industrial Strategy for Abatement

DATA SYSTEMS

USER'S GUIDE

MIDES AND TOXDATA

- MARCH, 1989 VERSION -

OVERHEAD #25

OVERHEAD #27

DISTRIBUTION AND SUPPORT

- MOE PROVIDES TO DISCHARGER:
  - CBT
  - MANUAL
  - TOXDATA PROGRAM
  - MIDES PROGRAM
  - CUSTOMIZED DISKS

- SOFTWARE LICENCE AGREEMENT
  - BETWEEN MINISTRY AND RECIPIENT
  - MINISTRY OWNS PROGRAM
  - DISTRIBUTION TO THIRD PARTY PERMISSION REQUIRED.

- CONTACT FOR SUPPORT IS REGIONAL OFFICE

- CONTRACT LABS GET:
  - COPIES
  - UPDATES
  - SUPPORT

  VIA DISCHARGER

OVERHEAD #28

MINISTRY OF THE ENVIRONMENT

LICENCE AGREEMENT

IMPORTANT: READ THIS CAREFULLY BEFORE OPENING THE ACCOMPANYING SEALED PACKAGE OF DISKS.

THIS LEGAL DOCUMENT IS AN AGREEMENT BETWEEN YOU, THE RECIPIENT, AND HER MAJESTY THE QUEEN IN RIGHT OF ONTARIO AS REPRESENTED BY THE MINISTRY OF THE ENVIRONMENT, REFERRED TO AS "THE MINISTRY" AFTER THIS.

BY OPENING THE SEALED PACKAGE OF DISKS, YOU ARE AGREEING TO BECOME BOUND BY THE TERMS OF THIS AGREEMENT, WHICH INCLUDES A SOFTWARE LICENCE AND ACKNOWLEDGEMENT.

IF YOU DO NOT AGREE TO THE TERMS OF THIS AGREEMENT, DO NOT OPEN THE SEALED PACKAGE OF DISKS. PROMPTLY RETURN THE UNOPENED PACKAGE AND THE ACCOMPANYING WRITTEN MATERIALS, TO THE MINISTRY.

(5) THE RECIPIENT SHALL NOT ASSIGN THIS AGREEMENT TO A THIRD PARTY WITHOUT THE PRIOR WRITTEN CONSENT OF THE MINISTRY.

(6) THE RECIPIENT MAY MAKE AS MANY COPIES OF THE PROGRAM AS IT REQUIRED FOR ITS INTERNAL USE. THE RECIPIENT SHALL NOT PRODUCE, STORE IN A RETRIEVAL SYSTEM, OR TRANSMIT, PHOTOCOPY OR RECORD BY ANY ELECTRONIC, MECHANICAL OR ANY OTHER MEANS THE PROGRAM FOR A THIRD PARTY WITHOUT PRIOR WRITTEN CONSENT OF THE MINISTRY.

A MISA Database for Ontario Petroleum Refineries

D.T. Chapman
Wastewater Technology Centre.

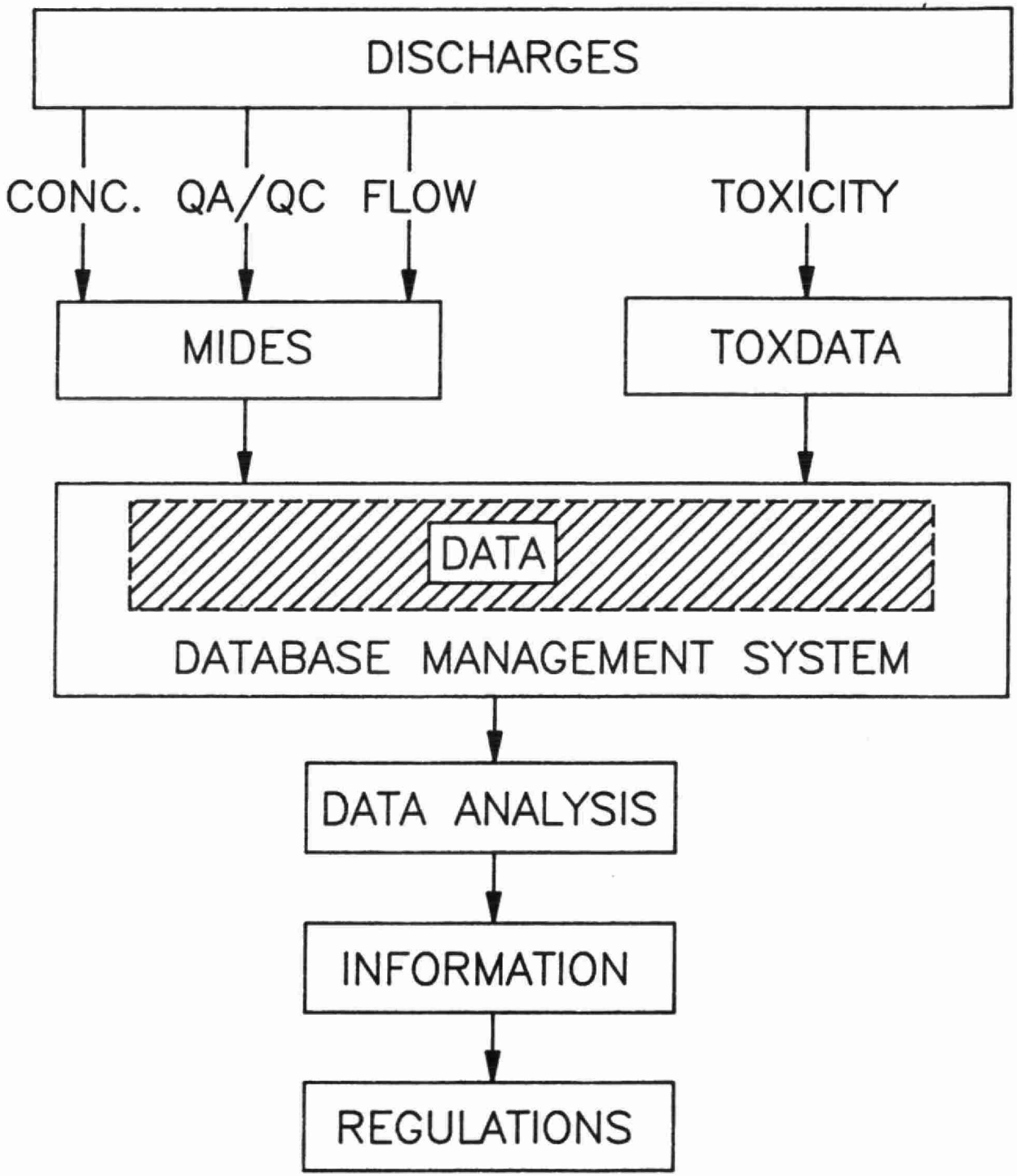
A summary was presented of a joint project conducted by the Ontario Petroleum Association (OPA) and the Wastewater Technology Centre (WTC) to develop, manage, and analyze a MISA database for the petroleum industry. Secondly, an overview was provided of the effluent standards developed by the U.S. Environmental Protection Agency to regulate American refineries. The overview identified how effluent data is analyzed to develop technology-based effluent regulations.

To create an industry-wide database for Ontario petroleum refineries, each of the refineries has forwarded diskettes containing MIDES EDT (Electronic Data Transfer) files of the MISA data to the WTC. Data is stripped from the EDT files and uploaded into a minicomputer. A minicomputer was used in preference to a micro-computer for database management and analysis because of the current superiority of the minicomputer in the areas of bulk data storage and speed of analysis. However, in the future, as 386 micro-computers become more common, it may be possible to manage such a database on these machines.

Reports have been generated summarizing results from 6 months of data collection and will be generated for 9 and 12 months of monitoring. The reports were developed using some custom FORTRAN programming and the use of a commercial statistical software package with a procedural language. The industry-wide reports contain three types of tabular summaries: load, concentration, and frequency-of-detection (FOD) tables. Load tables display the average mass discharge in kg/day of each of the 17 parameters which are monitored three-times per week or more at petroleum refineries under the MISA monitoring regulations. Because an individual refinery may have more than one type of discharge (ie. storm flow), all discharges of the same type are grouped together to determine loads in this table. Concentration tables display the mean and the coefficient of variation (expressed as a percentage) of concentrations of the frequently monitored parameters. The coefficient of variation, the standard deviation divided by the mean, is a useful statistic for comparing the variation or degree of spread between parameters with different concentration ranges. FOD tables display results for the 144 trace compounds which are monitored quarterly (for process effluent) or yearly (for landfarm leachate). FOD values, expressed as percentages, are the ratio of the number of samples with concentrations greater than the detection limit to the total number of samples. In other words, the FOD addresses the question: what percentage of the time did we find the compound when we looked for it?

Under the joint OPA/WTC study, future database management activities will include developing rejection criteria for data qualified by MIDES comment codes, analyzing field QC results (spikes, blanks, and replicates), developing procedures for calculating mass loadings per unit of production, and generating appropriate graphical displays. The overall objective is to employ clear, systematic, and consistent procedures for reporting and presenting MISA monitoring data for the petroleum refining sector.

A MISA DATABASE
for
ONTARIO PETROLEUM REFINERIES


DISCHARGES
CONC.
QA/QC
FLOW
TOXICITY
MIDES
TOXDATA
DATA
DATABASE MANAGEMENT SYSTEM
DATA ANALYSIS
INFORMATION
REGULATIONS

U.S. EPA REGULATIONS:

BPT:

- COD
- Sulfides
- Ammonia
- Phenolics
- Total Chromium
- Hex. Chromium
- BOD
- TSS
- Oil & Grease
- pH

BAT:

- COD
- Sulfides
- Ammonia
- Phenolics*
- Total Chromium*
- Hex. Chromium*

U.S EPA REGULATIONS:

END-OF-PIPE TREATMENT MODEL:

- Sour Water Stripping;
- Neutralization;
- Gravity Oil/Water Separation;
- Treatment of Cont. Storm Water;
- Sec. Oil/Water Separation;
- Biological Treatment;
- Granular Filtration;

U.S EPA REGULATIONS:

1.) FORM OF LIMITS:

- Mass Discharge of Pollutant;
- Max. Monthly Aver.;
- Max. Daily Aver.;

2.) CALCULATION OF LIMITS:

Limit = Allow Flow * Allow Conc. * V.F.

Allow Flow = Feedstock Capacity * Allow discharge;

Allow Conc. = "aver. of best";

V.F.: based on 50th, 95th & 99th percentiles.

MISA MONITORING:
ONTARIO REFINERIES

OWNER:	DISCHARGES TO:	TYPE:
Esso Petroleum Canada	St. Clair R.	Integrated
Petro-Canada (M)	Lake Ontario	Lube
Petro-Canada (O)	Lake Ontario	Cracking
Petrosar	St. Clair R.	Petrochemical
Shell Canada	St. Clair R.	Cracking & Chemical
Suncor	St. Clair R.	Cracking
McColl-Frontenac	Lake Erie	Cracking

MISA MONITORING:

ONTARIO PETROLEUM REFINERIES

DISCHARGES MONITORED:

- Process Effluent;
- Once-Through Cooling Water;
- Landfarm Leachate;
- Storm Water;
- Emergency Overflows;
- (Intake Water).

MISA MONITORING:

ONTARIO PETROLEUM REFINERIES

MONITORING PROGRAM:

1.) Continuous flows:

- process effluent:
  - daily: pH, VSS, phenols
  - 3/week: 17 parameters
  - 1/month: 2 toxicity tests
  - 1/quarter: 144 trace compounds
- once-through cooling water:
  - 1/month 17 parameters & 2 toxicity tests
- landfarm leachate:
  - 1/year: 144 trace compounds

2.) Episodic discharges (stormwater, emergency overflows):

- during discharge: 17 parameters

3.) Other: QA/QC: blanks, spikes, duplicates.

MISA MONITORING:

ONTARIO PETROLEUM REFINERIES

DATA ENTRY:

1.) TOXDATA:

2.) MIDES:

- Ease of Learning
- Data Entry
- Generation of Electronic Data Transfer (EDT) File

3.) Interface to Lab Information Management (LIM) System:

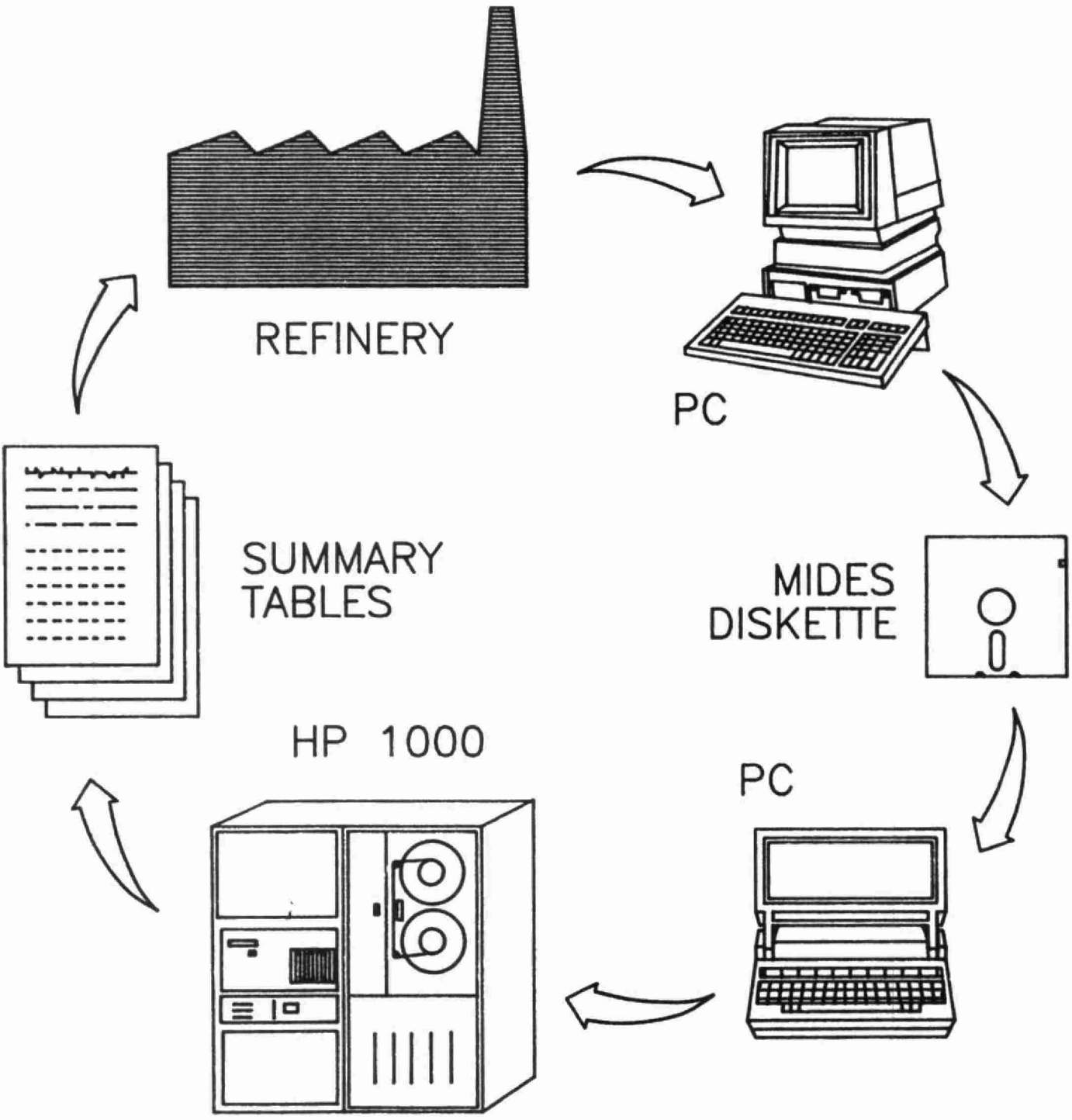
OPA/WTC STUDY:

STUDY OBJECTIVES:

- Develop & manage a comprehensive computer database;
- Provide summary reports:
  - for each refinery,
  - industry-wide comparison.
- Analyze & interpret data.

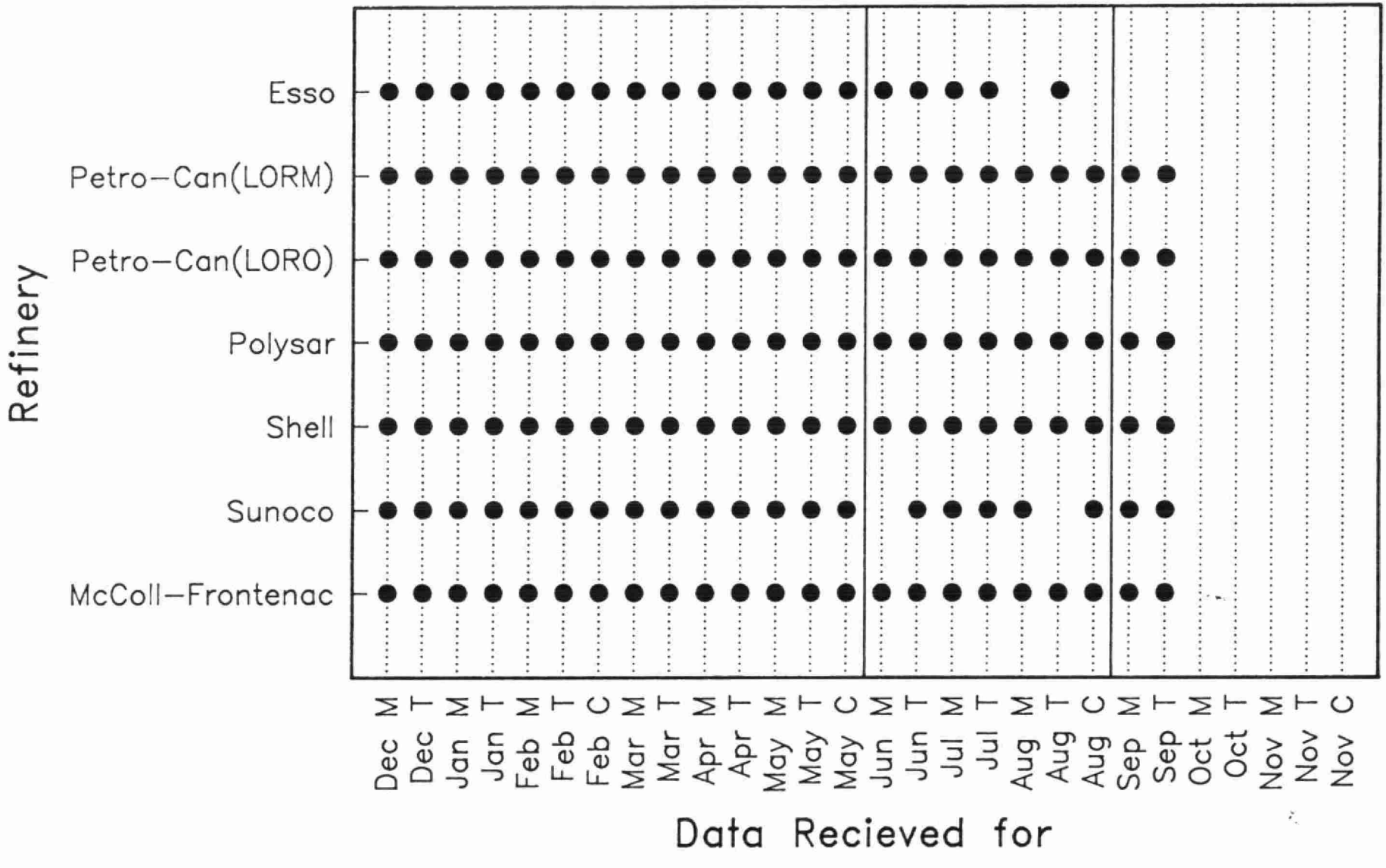
OPA/WTC STUDY:

METHODOLOGY



/OPA/COMMON/OPA.GRF

Reported Data from OPA as of NOV. 22, 1989



OPA/WTC STUDY:

Report Type: LOADING

Streams: Intake
Process Effluent
Landfarm Leachate
Storm Flows
Emergency Overflows
Cooling Water

Parameter	Refinery #1 .... (kg/day)	Refinery #7 (kg/day)	Average (kg/day)
Flow (1000 m3/day)	xxx.xx	xxx.xx	xxx.xx
TSS	xx.xx ...		
VSS	xx.xx		
Phenolics (4AAP)	xx.xx		
Oil & Grease	.		
Ammonia + Ammonium	.		
DOC			
TOC	.		
Total P			
Sulphide			
Chromium			
Zinc			
Benzene			
Ethylbenzene			
Toluene			
o-xylene			
m- & p-xylene	xx.xx ...		

OPA/WTC STUDY:

Report Type: CONCENTRATION

Streams: Intake
Process Effluent
Landfarm Leachate
Storm Flows
Emergency Overflows
Cooling Water

Parameter		Refinery #1	Average	Units
TSS	(mean)	x.xx ...		mg/L
	(c.v.)	x.xx		
VSS	(mean)	x.xx		mg/L
	(c.v)	x.xx		
.				
.				
.				
m- & p-xylene				
	(mean)	x.xx ...		µg/L
	(c.v)	x.xx ...		

OPA/WTC STUDY:

Report Type: FOD

Streams: Intake
Process Effluent

Parameter	Refinery #1	Refinery #7	Average
(17 Parameters)			
TSS	xx		
.			
.			
.			
No. Non-Conv. Found:			
Metals, etc.	x		
Organics	x		
(144 Parameters):			
Metals			
Aluminum	xx ...		
Beryllium	xx ...		
.	.		
.	.		
Hydrides			
Antimony			
.			
.			
PCBs Total	xx ...		

OPA/WTC STUDY:

EXAMINATION OF INDUSTRY-WIDE DATA TABLES:

- Missing data?
- Frequency of data collection?
- Higher than industry average?
- Lower than industry average?

Summary (Dec. - May)

	Discharges (1000 m^3/day)					
Refinery:	Proc.	Land.	Storm	Emer.	Cool	Tot.
Esso (Sarnia)	26	-	-	-	119	145
Petro-Can. (LORM)	9	-	-	-	104	113
Petro-Can. (LORO)	5	-	-	-	-	5
Petrosar (Cor.)	6	-	2	-	-	8
Shell (Sarnia)	12	-	7	-	137	156
Sunoco (Sarnia)	19	-	-	-	68	87
McColl-Frontenac	7	-	2	-	-	9

Trace Compounds in Process Effluents (Dec. - May)
(Excludes Conventionals)

Refinery:	Intake:	Process:
Refinery #1:	2	8
Refinery #2:	8	17
Refinery #3:	-	31
Refinery #4:	7	9
Refinery #5:	8	9
Refinery #6:	4	6
Refinery #7:	-	15
Average:	5.8	13.6

Trace Compounds In Intake & Process Effluent at 2 or More Plants (Excluding Conventionals)

Class:	No. Monitored:	No. Found:	
		Intake:	Process Eff:
Metals, Hydrides, etc.	15	5	13
Trace Organics	108	3	8

OPA/WTC STUDY:

FUTURE ACTIVITIES:

- Develop & distribute 9- & 12- month summaries;
- MIDES Comments: Criteria for data rejection;
  Comment Codes: <, >, <T, <TE, <W, <WE
- Analysis of QA/QC results;
- Procedure for calculating mass loadings per unit of production;
- Improved techniques for summarizing toxicity data;
- Graphical data displays.

SUMMARY:

- Data is <u>not</u> Information
- U.S. EPA Regulations;
- OPA/WTC Project:
  - Objectives
  - Methodology
  - Preliminary Results.

MOCHA

MISA
Organic
CHArcterization
Data System

Stephen Davies
Drinking Water Organics Section
Laboratory Services Branch

ORGANIC CHARACTERIZATION IN THE MISA PROGRAM



- The MISA program requires that Industry identify as best possible all organic compounds present in their effluent
- This process is known as "organic characterization", "open-scan", or "full-scan" analysis
- The Laboratory Services Branch of MOE also performs organic characterizations, mainly to allow for comparison (audit) of industry's results
- The results of these analyses must be reported back to MOE's MISA office or central database in a manner analogous to the reporting of target compound data

HOW CHARACTERIZATION DIFFERS FROM TARGET COMPOUND ANALYSIS



- Output from an organic characterization has variable format
- Analytes are not know before the analysis begins
- The number of analytes found can vary widely
- Organic characterization results are semi-quantitative

RESULTS OF A CHARACTERIZATION ANALYSIS



- Compounds positively identified
- Compounds with some identifiable functional groups
- Complete unknowns

Characterization compound identifications may be made at varying degrees of specificity and confidence

Under MISA, four "identification classes" are recognized:

1) Confirmed
2) Provisional
3) Compound Class
4) Unknown

1) CONFIRMED IDENTIFICATION



Identical match between mass spectrum and retention time of unknown analyte compared to an authentic standard of the identified compound

2) PROVISIONAL IDENTIFICATION



- Compounds identified solely by matching unknown and reference mass spectra
- An authentic standard has not been analyzed (under the same conditions of the unknown)

3) COMPOUND CLASS IDENTIFICATION



- Sufficient information doesn't exist for compound identification
- Mass spectra are indicative of a specific molecular structure
- Includes cases where no reference spectra closely match unknown
- Compound class identification may be achieved by manual interpretation of the mass spectra

4) UNKNOWN IDENTIFICATION



- Mass spectra cannot be identified without more information
- No reference spectra closely match unknown spectra
- No specific compound class structural features are evident

MOCHA: MISA ORGANIC CHARACTERIZATION



Question: What is MOCHA?

Answer: MOCHA is the proposed format for reporting MISA characterization data

The basic structure of the reporting format is a modified version of a template distributed in a "green report" entitled:

"Techniques for the Gas Chromatography - Mass Spectrometry Identification of Organic Compounds in Effluents", November 1988

Ray E. Clement, and Vince Y. Taguchi

MOCHA: MISA ORGANIC CHARACTERIZATION



Question: What is the relationship of MOCHA to MIDES?

Answer:

- The MIDES program is also a MISA data entry system
- Clipper (compiled dBASE III+) program
- Executes on IBM-compatible microcomputers
- Facilitates the collection of MISA target compound data
- Transmittal to a central Ministry database system (SIS)
- Specific for target compound analyses

APPROACH TO THE IMPLEMENTATION OF MOCHA



Phase 1: Data entry module

Phase 2: Centralized database

SCHEDULE FOR IMPLEMENTING MOCHA



PHASE 1: DATA ENTRY MODULE

	1989					1990		
Month	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar
Week	12345	1234	1234	12345	1234	1234	1234	1234
Task								
Data entry specs	XXXXX							
RFP tendered		XXXX						
Vendor selection			X	X				
Programming/data entry				XXXX	XXXX	XX		
Testing of data entry						XX		
Training re data entry						X		

MOCHA DATA ENTRY SYSTEM MUST ...



- Be able to recognize reports of varying numbers of analytes, and also allow for compound identifiers which are typed in
- The system must also allow for compound classes to be accepted (ie. aromatic hydrocarbon etc.), as well as explicit identities
(ie. 2,3,7,8-Tetrachlorodibenzo-p-dioxin etc.)

DATA ENTRY USING MOCHA



TWO DISCRETE EVENTS:

1) **Preparation of a paper template containing analytical data**
2) **The entry of data from the template into the MOCHA program**

Chemical Abstract Service (CAS) registry number

- **uniquely named for provisional or confirmed identifications**

MISA CHARACTERIZATION REPORT

SAMPLE NO. : _____ DATE SAMPLED : _____

DATE ANALYZED : _____

GC-MS SYSTEM : _____

COLUMN : _____

TEMPERATURE PROGRAM : _____

INTERNAL STANDARD : _____

RETENTION TIME : _____

ANALYSIS TYPE : _____

CONCENTRATION UNITS : _____

REPORTING OF SYSTEM CHARACTERISTICS



The GC-MS data system must be identified, as well as the experimental conditions under which the analysis was performed. This includes data on temperature programming and type of column utilized

MISA CHARACTERIZATION REPORT

SAMPLE NO. : MY??-????

DATE SAMPLED : 89 04 25
DATE ANALYZED : 89 05 03

GC-MS : Hewlett-Packard 5890 GC/5970 MSD

COLUMN : DB-5 60m 0.25mm I.D. 1.0u

TEMPERATURE PROGRAM : 30°C to 100°C at 8°C/min. to 150°C at 3°C/min. to 220°C at 20°C/min. and hold 7 min.

INTERNAL STANDARD NAME: d_{10}-ethylbenzene

RETENTION TIME : min.

ANALYSIS TYPE : Volatile organics

REPORTING CONVENTIONS



- Semi-quantitative concentrations
- Results can be reported in either ppb or ppm
- A four number wide integer numeric field (no decimals) can be used to store the concentration values
- "A-" (approximate) prefix to be added to the number entered
- Concentration reported contains only one significant figure and is padded with zeros to indicate order of magnitude

SORTED ORDER OF COMPOUND ENTRIES



Compounds should be entered in ascending order using retention time (in minutes)

FIELD SIZES

- "##.##" signs denote place-holders for the fields on the template
- The "Identity field" should be as large as possible (much larger than shown on the example template) in order to accommodate long chemical names. This will require that two lines or more are used for each name

ENTRY NO.	RET. TIME	CONC.	CAS REGISTRY NUMBER	ID CLASS	REF. LIB.	MATCH NO.
	Compound Name		(nomenclature unimportant if CAS # known)			
1	2.56	A-400	[1740198] Dehydroabietic acid	C	NBS	850
2	3.19	A-10	[120832] 2,6 Dichlorophenol	P	EPI	825
3	5.63	A-50	Unidentified	U	---	---
4	7.87	A-6000	[106445] p-Cresol	P	W	960
5	12.56	A-60	Trichlorobenzene	CL	MI	---

MATCH NUMBER



The match number is an integer number used to describe the closeness of the compound in question to one stored in a computerized database called a “reference library”. The reference library used should be specified

ENTRY OF ANALYTES IDENTIFIED AT THE COMPOUND CLASS LEVEL



- CAS numbers cannot be used for identification
- A list of group names (functional groups) has been devised
- The user may scroll through the list and hits a key to select structural group names from the list
- Multiple groups can be associated with entry of a single compound

COMPOUND CLASSES USED IN CHARACTERIZING ORGANICS IN EFFLUENTS



1. Hydrocarbons
   for example:
   Hydrocarbon (Saturated) (Alkyl)
   Hydrocarbon (Unsaturated) (Alkenyl) (Alkynyl)
   Hydrocarbon (Cyclic)
   Hydrocarbon (Aromatic) (Benzene)
   Hydrocarbon (Polycyclic Aromatic)
2. Carbocyclic Acids and Derivatives
3. Heteocyclics
4. Organohalides
5. Oxygen - containing
6. Nitrogen - containing
7. Sulphur - containing
8. Phosphorous - containing
9. Organometallics
10. Steroids
11. Unknowns

ENTRY NO.	RET. TIME	CONC.	IDENTITY	ID CLASS	REF. LIB.	MATCH NO.
1	6.1	A-9	polyethylene glycol	CL	---	---
2	9.5	A-9	ether alcohol	CL	---	---
3	11.0	A-3	hydrocarbon	CL	---	---
4	12.5	A-6	unidentified	U	---	---
5	13.6	A-1000	[112-34-5] 2-(2-butoxyethoxy) ethanol	P	NBS	870
6	15.0	A-60	[143-22-6] 2-(2-(2-butoxyethoxy)ethoxy) ethanol	P	NBS	880
7	15.3	A-3	ether alcohol	CL	---	---



USAGE OF CHARACTERIZATION DATA

NOT USED FOR:



- Semi-quantitative data should not be used to calculate loadings
- Semi-quantitative data should not be used for statistical tests (with the exception of ranking presence/absence types of tests)

USED FOR:

- Identification of analytes not on the MISA target compound list (adding analytes to the MISA target compound list)
- "De-listing" of compounds from the MISA target compound list

SECTION FOUR

SESSION THREE - QUALITY MANAGEMENT

CHAIRPERSON: MR. SERGE VILLARD, MOE

LABORATORY QA/QC	-	D. KING, MOE
LABORATORY INSPECTIONS	-	C. DOEHLER, MOE
OPA INTERCOMPARISON REVIEW	-	A. MAYNARD, ASL
MOE ROUND ROBIN PROGRAM	-	S. CUSSION, MOE



MISA

Municipal/Industrial Strategy for Abatement

MISA LABORATORIES

QUALITY ASSURANCE & ANALYTICAL METHODS WORKSHOP

CONTROLLING QUALITY IN THE ANALYTICAL LABORATORY

Donald King
Quality Assurance Office
Laboratory Services Branch

QUALITY MANAGEMENT ISSUES



- Quality & Management
- Laboratory Operations
- Measurement Processes
- Control
- Performance Monitoring
- MISA Quality Management

QUALITY & MANAGEMENT



QUALITY IMPLIES:

- Suitability for use
- Conformance to specifications

MANAGEMENT IMPLIES:

- Policies (requirements)
- Guidelines (framework)
- Protocols (what to do)
- Procedures (how to do it)
- Audits (verification)

QUALITY & MANAGEMENT

AREAS REQUIRING MANAGEMENT



- Sample Processing
- Workload & Throughput
- Analytical Methodology
- Records and Data
- Reporting
- Quality

QUALITY & MANAGEMENT



QUALITY MUST BE MANAGED

- Specifications
- Checking Procedures
- Evaluation Techniques
- Remedial Action
- Documentation

QUALITY MANAGEMENT ISSUES



- Quality & Management
- Laboratory Operations
- Measurement Processes
- Control
- Performance Monitoring
- MISA Quality Management

LABORATORY OPERATIONS

FACTORS AFFECTING DATA QUALITY



- Facilities and Equipment
- Instrumentation and Standards
- Supplies and Services
- Samples and Method
- People
- Procedures

LABORATORY OPERATIONS

PARTICULAR AREAS OF CONCERN



- Lab cleanliness
- Quality of supplies
- Selection of method
- Sample suitability
- Analyst experience
- Proper records

QUALITY MANAGEMENT ISSUES



- Quality & Management
- Laboratory Operations
- Measurement Processes
- Control
- Performance Monitoring
- MISA Quality Management

MEASUREMENT PROCESSES



PROPER MEASUREMENT REQUIRES

- Sample decomposition
- Isolation of analyte
- Adequate identification
- Efficient recovery
- Precise measurement
- Accurate calibration

MEASUREMENT PROCESSES



VARIABILITY AND ERROR

- Natural variability
  - method ruggedness
  - sample homogeneity
  - analyst skill
- Systematic error
- Non-systematic error

MEASUREMENT PROCESSES



SOURCES OF SYSTEMATIC ERROR

- Inaccurate standards
- Inaccurate calibration
- Uncontrolled blank correction
- Method bias

SOURCES OF NON-SYSTEMATIC ERROR

- Chronic lab contamination
- Sample matrix effects
- Inadequate method recovery
- Sloppy technique

QUALITY MANAGEMENT ISSUES



- Quality & Management
- Laboratory Operations
- Measurement Processes
- Control
- Performance Monitoring
- MISA Quality Management

CONTROL



CONTROL IMPLIES

- Definition of acceptability
- Predictability
- Warning limits (1:20)
- Control limits (1:200)
- Defect detection (charting)
- Proper & timely action

CONTROL



CONTROL CHARTS

- Monitor trends over time
- Incorporate performance spec's
- Facilitate performance evaluation
- Document performance achieved

QUALITY MANAGEMENT ISSUES



- Quality & Management
- Laboratory Operations
- Measurement Processes
- Control
- Performance Monitoring
- MISA Quality Management

PERFORMANCE MONITORING

PERFORMANCE CHARACTERISTICS



- Repeatability (ability today)
- Reproducibility (between day)
- Precision (between lab)
- Bias (method/standards)
- Accuracy (external reference)

PERFORMANCE MONITORING



MEASURES OF PERFORMANCE

- Replicate analysis of samples
- Calibration control standards
- Method blanks
- Method recovery control samples
- Recovery of spiked samples

QUALITY MANAGEMENT ISSUES



- Quality & Management
- Laboratory Operations
- Measurement Processes
- Control
- Performance Monitoring
- MISA Quality Management

PERFORMANCE MONITORING

VERIFICATION OF PERFORMANCE



- Standard Reference Materials
  - pure compounds
  - certified standards
  - natural materials
- Interlaboratory Comparison
- Audits
  - performance checks
  - laboratory inspections

MISA QUALITY MANAGEMENT



- Quality Management
  - due diligence
- Laboratory Operations
  - code of practice
- Measurement Processes
  - method principles, MDL's

MISA QUALITY MANAGEMENT



- Control
  - minimum lab & field QA/QC
- Performance Monitoring
  - field audit samples
  - laboratory inspections
  - round-robins

MOE LABORATORY INSPECTIONS

Cathy Doehler
Quality Assurance Office
Laboratory Services Branch
Environment Ontario

MISA LABORATORY INSPECTIONS



- Purpose / Scope
- Personnel / Frequency
- Implementation
- Conclusions / Follow-up

MISA LABORATORY INSPECTIONS

REGULATORY INSPECTION

Purpose - to evaluate and verify compliance status to regulatory statutes ex. Ontario Regulation 695/88 (amended to 533/89)

Scope - evaluation limited to specific requirements defined in regulations

MISA LABORATORY INSPECTIONS



Satisfactory Laboratory Inspections Ensure Regulatory Compliance

They Do Not Imply MOE Certification

MISA LABORATORY INSPECTIONS

FACTORS THAT INITIATE AN INSPECTION



- ▲ regulatory compliance
- ▲ data quality problem shown by submitted data
- ▲ follow-up action when compliance problem documented

MISA LABORATORY INSPECTION

INSPECTION PERSONNEL

- MOE LSB Quality Assurance staff
- MOE regional personnel

FREQUENCY

- Initial report site visit
- Laboratory inspection
- Follow-up visit

MISA LABORATORY INSPECTION

LABORATORY INSPECTIONS - AREAS OF CONCERN



- ▲ sampling (effect on analytical results)
- ▲ sample pretreatment and preservation
- ▲ storage and transport
- ▲ sample analysis / quality assurance
- ▲ data reporting and interpretation
- ▲ staffing, safety, housekeeping, facilities / equipment

MISA LABORATORY INSPECTION

SAMPLING

- ▲ sampler maintenance
- ▲ sampling conditions
- ▲ sampling schedule
- ▲ methods
- ▲ container labelling

MISA LABORATORY INSPECTION

SAMPLE PRETREATMENT AND PRESERVATION



- ▲ clean-up or specialized extraction performed
- ▲ container cleanliness / pretreatment
- ▲ preservation instructions / recipes / quality control
- ▲ pH must fall within regulation limits
- ▲ pre-charged sampler bottles

SAMPLE STORAGE AND TRANSPORT

- ▲ maintain samples between 0-10°C / monitor
- ▲ analytical start time tracking
- ▲ sample routing

MISA LABORATORY INSPECTION

SAMPLE ANALYSIS / QUALITY ASSURANCE



- ▲ methods
- ▲ calibration curves
- ▲ standards, calibration / SRMs
- ▲ QC analysis, frequency / monitoring quality
- ▲ recovery
- ▲ MDLs
- ▲ control limits, daily calibration / method blank
- ▲ intercomparison studies, methods / labs
- ▲ performance reports

MISA LABORATORY INSPECTION

DATA REPORTING AND INTERPRETATION

- ▲ initial report
- ▲ result screening / approval / release
- ▲ data interpretation of open / elemental scans
- ▲ traceability of results
- ▲ merging / coordination of industrial and commercial lab data

MISA LABORATORY INSPECTION

STAFFING / SAFETY / FACILITIES / EQUIPMENT



- ▲ organization chart pertinent to MISA analysis
- ▲ staff qualifications / training
- ▲ chemical spill / emergency plans
- ▲ facility / equipment maintenance

MISA LABORATORY INSPECTION

CONCLUSIONS / FOLLOW-UP

- ▲ summaries to MOE, WRB, region, industry
- ▲ copy of checklist to laboratory, LSB
- ▲ follow-up inspection
- ▲ refer to IEB for investigation

MISA LABORATORY INSPECTION

PURPOSE OF MISA MONITORING REGULATION



"To establish a data base on effluent quality...that, along with other pertinent information, will be used in the development of effluent limits"

ASL

PAPER ONTARIO PETROLEUM ASSOCIATION: INTER-COMPARISON REVIEW

By: Allan William Maynard
ASL Analytical Service Laboratories Ltd.

Presented At The Toronto Airport Hilton Hotel, November, 1989.

INTRODUCTION

- As mentioned I have had the pleasure of working with the Petroleum Association for Conservation of the Canadian Environment (PACE), since 1980.

- The work we have done for PACE has been very satisfying in that PACE was supportive of all our efforts towards good quality assurance through the programs.

- All of the studies involved refinery wastewaters and we definitely feel that the programs have truly defined what is present and what is not present in refinery wastewaters.

- As a result of this research the Petroleum Association were well prepared for the MISA program. However it is a sense of frustration on my part to see how extensive their monitoring programs are within the legislation because I feel in many ways that the work they are having to do now is somewhat redundant.

- However I suppose political decisions were made and the good technical work was not used to its maximum extent.

analytical service laboratories ltd.
CONSULTING CHEMISTS & ANALYSTS
1650 Pandora Street
Vancouver, B.C. • V5L 1L6
Fax (604) 253-6700 • Tel. (604) 253-4188

- As I mentioned all of the wastewater programs we did do on behalf of PACE involved a large quality assurance/quality control component.

- For these reasons we obtained a good handle on the analytical variability associated with characterization type analyses.

- In working with this information I put together, in 1987, a paper dealing with analytical variability and I have been asked to present this paper at a number of conferences in Canada and the United States.

- It would seem that all those involved in environmental monitoring programs are concerned about analytical variability and it has become necessary to obtain a very good comprehension of this component of monitoring.

BRIEF DESCRIPTION OF ANALYTICAL VARIABILITY

- Before I discuss some of the more recent programs that PACE or the OPA have sponsored, I want to present some information that provides the necessary perspective on chemical analyses and the analytical variability associated with these chemical analyses. This is the kind of information that I have presented to industry and government and it has proved useful to them in obtaining the required understanding.

- SLIDE 1 - See next point

- This first slide is the way in which the U.S. Department of Food and Drugs evaluate analysis procedures, and these are based on these characteristics:
  - -- Reliability
  - -- Applicability - to a wide variety of sample types
  - -- Practicality - with respect to cost, time and training constraints
- SLIDE 2 - See next point

- Reliability is clearly the overriding consideration and it is determined by establishing a methods
  - -- reproduceability - which is the between laboratory precision of an analysis determined by inter-laboratory studies.
  - -- repeatability - which is within laboratory precision and defines the ability of one lab to check itself.
  - -- systematic error or accuracy
  - -- specificity - to measure an analyte without interference from other chemicals
  - -- sensitivity or detection limit

- One of my concerns with the MISA Program is the issue of method detection limits. I feel that there has been entirely too much focus on the issue of detection limits and not enough discussion on the overall reproducability of the analyses.

- SLIDE 3 - See Appendix.

- One slide I do like to show to people who are not involved in analyses is this one which shows the different types of analyses, some of which are very accurate and precise- others for which that is not the case. We must obtain this information for all the analysis groups within MISA.

- SLIDE 4 - See Next Point

- Now in considering the characteristics of an analysis it then stands to reason that the analysis procedures must then be evaluated in terms of the information that is required. The AOAC in the U.S. evaluate analysis for three major purposes or "steps" in an analytical program:

  - Step 1 is to survey a field to determine the extent of the problem, I like to call this characterization. A high degree of accuracy and precision, while definitely desirable, is not necessarily required as the object is to define whether or not an analyte or analytes are present and whether the levels are high or low. In many respects, the pre-regulation programs undertaken by the industries would be the "characterization programs".

  - Step 2 is then to monitor, this requires numerous determinations with practical methods that can provide sufficient information in the time allotted.

- Within the context of effluent monitoring, this stage should establish the variability of discharge and the relationship among parameters. The present monitoring regulation is indeed the monitoring stage but in many respects I feel it is too extensive and is really attempting to do more characterization along with the monitoring.

- The final monitoring requirement is compliance monitoring which requires a high degree of accuracy and precision. Here it is necessary to select the few parameters that are analysed by well defined and, hopefully, validated methods.

INFORMATION AVAILABLE PRIOR TO MISA

- Now that I have discussed a little bit of information about characteristics of methods and purposes for applying various methods, I would like to briefly outline what information was available to us prior to the onset of the MISA regulation.

- As I stated all of the PACE studies did involve a high level of QA/QC and some of this within lab variability information, did indicate that analytical variability was a significant factor in interpreting the results.

- The only published information was the EPA criteria and information published by the Chemical Manufacturers Association.

- SLIDE 5

- This next slide shows the EPA published acceptance criteria for Priority Pollutants. I have just shown some typical examples in the slide. This is the spike and recovery requirements published with methods 624 for volatiles and 625 for extractables.

- The EPA recognized a high degree of variability for certain parameters, for instance, for vinyl chloride a tolerance of more than 100% variability was expected, for a 20 ppb spiked water a result of just detected to 43 μg/L is acceptable. Benzene, on the other hand, is expected to be less variable at the 20 ppb.

- This kind of information that was published by EPA was of such concern to the Chemical Manufacturers Association whose members were being regulated by the EPA that they initiated their own study.

- SLIDE 6

- The U.S. based Chemical Manufacturers Association presented their findings in which three highly reputable EPA contract labs were used to analyse spiked groundwater. Some typical results are shown, two showing reasonable precision and two showing poor precision.

- One of the alarming aspects of the CMA study was that while quantitative agreement was in some cases poor, there were parameters for which qualitative agreement was not achieved. In other words there were false positives and false negatives.

- What this study demonstrated is the many of the EPA Priority Pollutants methods are not adequate for compliance monitoring. Now I realize the methods have improved over the past three to four years but there has been very little published in this regard.

- This is why the Petroleum Association has sponsored, so far, two studies and are looking at doing other work.

SUMMARY OF PACE STUDIES

- SLIDE 7

- The Petroleum Association or PACE have sponsored two studies to date, one concerning conventional parameters and one concerning volatile organics.

- SLIDE 8

- The first PACE study was an inter-lab study on conventionals and we looked at analysis for suspended solids, oil and grease, phenols, dissolved organic carbon, chemical oxygen demand, ammonia nitrogen, and three metals.

- SLIDE 9

- The types of samples that were analysed were water, spiked water, effluent and spiked effluent.

- SLIDE 10

- The methodology to prepare the samples was, in my opinion, well thought out with significant input obtained from the MOE lab people. We prepared all the samples at Dearborn Environmental Consultants laboratory in Mississauga.

- Some samples involved a lot of mixing and these were mixed in large mixing tanks with high speed agitation.

- For oil & grease the bottles were individually spiked with a solution of acetone containing a known quantity of oil.

- Five of each of the samples were randomly selected and analysed internally, either in our laboratory in Vancouver

or in the Dearborn laboratory. This was to obtain a within lab result.

- There were thirteen participating laboratories.
  - Two of which were government laboratories
  - Seven were refinery laboratories
  - Four were commercial laboratories

- SLIDE 11

- In some cases, as shown in this slide, the results were quite encouraging.

- For the parameters, suspended solids, COD, and metals, the coefficients of variation or standard deviation were about 20% or less.

- Blanks were submitted as samples and in only few isolated instances were there false positive values reported.

- In other cases a higher degree of variability and incidence of false positives were reported.

- We were not really surprised at these results for oil and grease and phenols showing variabilities above 45% and a high incidence of false positives.

- In other words, five out of twelve laboratories reported oil and grease in distilled water to levels as high 11 mg/L.

- We felt on the basis of these results that the method detection limits should be raised for these tests to 5 mg/L for oil and grease and 5 μg/l for the total phenols test. We do not feel that the results below those levels can be relied upon - especially in the case of oil and grease- there is no use in forcing the MDL lower than 5. With

phenols there may be a rational for working towards reliable data in this range.

- SLIDE 12

- The next inter-laboratory study carried out was on volatiles. We looked at benzene, toluene, ethylbenzene and xylenes, trichloroethane and because of the results on oil and grease in the previous study we looked at three additional samples for oil and grease.

  Aromatics -- because these are the 3X weekly
  111 TCE -- has been found in refinery intake and consequently effluent samples

- SLIDE 13

- The types of samples that we looked at in the second study were:

  - refinery effluent
  - spiked effluent (spiked in the range of 4.7 to 14 ppb) of the various contaminants
  - blank surface water - and here we used water collected from the Seymour River in Vancouver above any type of development. This is well aerated water and we felt this would represent a good blank surface water.
  - spiked surface water - (the same surface water was spiked in the range of 4.7 to 7.5 ppb)
  - St Clair river water was also analysed.

- SLIDE 14

- The methodology involved:
  - spiking the individual vials separately

- dispensing the unspiked materials, the surface waters and effluent, using an oven baked dispensing bottle.
- All solutions during spiking and handling, and so on were kept at less than 8°C.
- again 5 samples were individually analysed internally
- in this study there were 16 laboratories, the same two government labs, a number of refinery labs and a number of commercial laboratories.

o Most of the results were unfortunately not detected and one of the conclusions that we make from this study is that the spiking probably should have been at higher levels.

-- The effluent was generally showing not detected levels.
-- The spiked effluent was showing not detected levels and I will discuss that in a moment.
-- The blank surface water was showing not detected levels.
-- The St. Clair was showing not detected levels.

o SLIDE 15

o This next slide shows the summary of results for the spiked effluent. For instance benzene was spiked at a level of 7.4 µg/L, the median result was not detected and the frequency of detection was three out of the nine laboratories that analysed for benzene.

o Toluene spiked at 11.2 µg/L, the median concentration was not detected and the frequency of detection was only one out of nine laboratories.

o Trichloroethane, on the other hand, the spike was at 4.7 µg/L and six out the seven laboratories detected it and the median concentration was 4.1 µg/L.

- The conclusion we drew from these results were that the volatile aromatics were biodegrading as soon as they were added to the effluent. Some of the laboratories analysed the sample within 24 hours of receipt and still showed undetected levels for these contaminants. Trichloroethane on the hand, is less biodegradable and was generally detected.

- This is an interesting result and could show that for the volatile aromatics the results must be analysed very quickly after collection, or preserved in some way.

- SLIDE 16

- The next slide shows the results of the spiked water and in these cases all of the spiked compounds were detected.
  -- Benzene for instance was spiked at 4.7 µg/L.
  -- All the laboratories detected benzene.
  -- Mean concentration was 4.5 µg/L and the standard deviation was 1.3 µg/L.
  -- Likewise with toluene the spike was at 4.7 µg/L, the mean was 4.6 and the standard deviation was 3.3 µg/L.

- So the results of the spiked water were much more encouraging with variabilities in the 25% to 50% at these spiked levels.

- SLIDE 17

- There were some common false positives, the most common being benzene, xylenes, chloroform and methylene chloride.

- SLIDE 18

- One of the concepts we introduced in the study was the concept of practical quantitation limit.

- There was a definite degree of variability at this low level of spiking.
- This kind of variability has been observed and reported by others working in the same field
- The EPA have therefore defined a practical quantitation limit as been the limit at which 80% of the labs obtain results at ±40% of the true value
- Three other published studies have shown that the PQL's are much higher than the MDL's
- This study confirms these findings

o We feel that with the MISA regulations there is a very strong emphasis on the use of MDL and it has been forgotten what the purpose of the MDL was. It is now expected by the regulatory people that the results on all samples must be reported using these MDL's. However when the MDL concept was initially introduced it was made clear that it was only a way of ensuring the ability of the laboratories to analyse for the contaminants at low levels. It was recognized that actual samples may have to have higher detection limits due to the need to dilute or possible interferences or matrix effects.

o I realize that these concerns can be covered by remark codes but I personally am very concerned about reporting data near water based MDL's and especially levels below these MDL's. I feel this concept is contrary to the objectives of analytical analysis to report "real" and reliable data.

o SLIDE 21

o Our final recommendations for further immediate studies would be to

- Look at this concept of biodegradation and the possible use of preservatives and,

- Develop samples at higher concentrations so a better estimate can be made of PQL.

o In Summary

-- I have outlined some background of work carried out on behalf of PACE and OPA.
-- I have outlined why there is concern for analytical variability.
-- I have reviewed the findings of 2 interlab studies carried out along with recommendations for further work.

o I would like to close by saying that the industry is still concerned about the issue of analytical variability and are hopeful that those of us in the analytical field can resolve this issue so that the data base generated by MISA will be meaningful and properly understood by those who must interpret them. We have this responsibility as chemical analysts to provide the necessary education in this regard.

o I congratulate the lab Services Branch for hosting this well organized and well attended session to allow these concerns to be discussed.

APPENDIX

SLIDES SHOWN

SLIDE 3

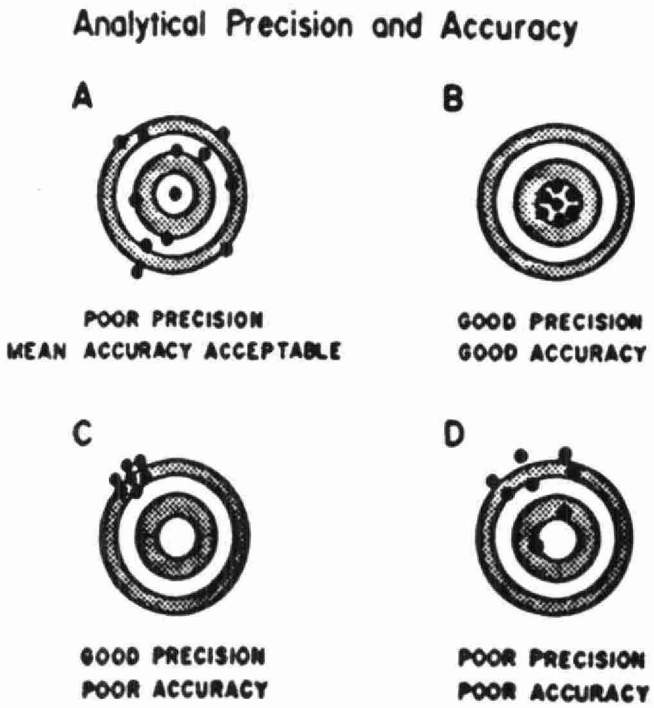


Figure 1. Relationship between precision and accuracy of analytical measurements

SLIDE 5

TABLE 5 EPA PRIORITY POLLUTANTS : RECOVERY OF SPIKED COMPOUNDS

PARAMETER	SPIKE LEVEL (µg/L)	RANGE (µg/L)
Vinyl Chloride	20	D - 43.5
Benzene	20	15.2 - 26.0
Pentachlorophenol	100	38.1 - 151.8
Phenol	100	16.6 - 100.0
Benzo-A-Pyrene	100	D - 195.
Crysene	100	D - 134.

Selected results from EPA, 1984 D = Detected

SLIDE 6

TABLE 6 : CMA ASSESSMENT STUDY

PARAMETERS	SPIKE LEVEL (µg/L)	RANGE (µg/L)	
Benzene	50	43. -	86.
Ethylbenzene	200	ND -	225.
Nitrophenol	300	11. -	765.
Chlorophenol	300	200. -	270.

Selected results from Stanko & Fortini, 1985

SLIDE 7

PACE : 2 INTERLABORATORY STUDIES

- CONVENTIONALS
- VOLATILE ORGANICS

SLIDE 8

PACE: INTERLAB STUDY ON CONVENTIONALS

- S. SOLIDS
- OIL & GREASE
- PHENOLS
- DOC
- COD
- AMMONIA N
- METALS - CU CR ZN

SLIDE 9

SAMPLE TYPES

- WATER
- SPIKED WATER
- EFFLUENT
- SPIKED EFFLUENT

SLIDE 10

METHODOLOGY

- MIXING -- 100 LITER MIXING TANK
- OIL & GREASE -- BOTTLES INDIVIDUALLY SPIKED
- 5 RANDOM SAMPLES -- ANALYZED INTERNALLY
- 13 PARTICIPATING LABS - RAPID DELIVERY

SLIDE 11

TABLE 1 RESULTS SUMMARY FOR PACE INTER-LABORATORY STUDY

No.	Parameter	"True" Value	Within-Lab Summary (n=5) Mean (or Med)*1	S.D.	"False" Positives	Inter-Lab Summary (n=7-13)*3 Mean (or Med)*1	S.D.	"False" Positives
1	Suspended Solids	<1.	(<1.0)	-	0	(<1.0)*2	-	1/12
2	" "	30.	29.33	0.82	-	22.12	4.07	-
3	" "	-	39.40	3.85	-	30.78	5.66	-
4	Oil & Grease	<1.	(<1.0)	-	0	(<1.0)	-	5/12
5	" "	X+22	16.75	2.22	-	12.90	11.30	-
6	" "	9	5.40	2.07	-	6.24	5.09	-
7	Phenols	-	0.039	0.004	-	0.040	0.023	-
8	"	0.01	0.010	0.001	-	0.013	0.006	-
9	"	<0.001	(<0.001)	-	0	(<0.001)	-	6/12
10	DOC C	<0.5	0.5	-	3	(0.5)	-	5/9
11	" C	15.0	15.42	0.20	-	17.13	3.91	-
12	" C	-	11.60	0.22	-	18.189	9.12	-
10	COD	<10.	(<10.)	-	0	(<10.)	-	2/8
11	"	37.5	33.42	2.42	-	39.48	7.09	-
12	"	-	86.60	3.72	-	88.73	19.69	-
13	Ammonia N	-	1.23	0.11	-	1.68	0.73	-
14	"	<0.2	(<0.01)	-	-	<0.01	-	4/13
15	"	0.60	0.58	0.014	-	0.71	0.36	-
16	Chromium Cr	<0.01	(<0.01)	-	0	(<0.02)	-	1/8
17	"	<0.01	(<0.01)	-	0	(<0.02)	-	1/8
18	"	0.27	0.276	0.005	-	0.295	0.111	-
16	Copper Cu	<0.01	(<0.005)	-	0	(<0.01)	-	1/7
17	"	0.07	0.068	0.001	-	0.075	0.014	-
18	"	0.1	0.100	0.001	-	0.106	0.016	-
16	Zinc Zn	(<0.01)	<0.005	-	0	(<0.010)	-	1/8
17	Zinc Zn	0.09	0.080	0.004	-	0.096	0.023	-
18	Zinc Zn	(<0.01)	<0.005	-	0	(<0.010)	-	1/8

DOC = Dissolved Organic Carbon COD = Chemical Oxygen Demand
SD = Standard Deviation
*1 When the sample analysed was actually a blank, a median (med) is reported (in brackets) rather than a mean. A standard deviation does not accompany the median.
*2 When the median is actually a less than detection, the most commonly reported detection limit is given.
*3 n = 7 to 13 since not all labs analysed for each parameter, the n for each parameter is given in the last false positives column.
True Value - was known for synthetic spiked samples and the distilled water sent as samples. (from Maynard & Daly 1988)

SLIDE 12

PACE: INTERLAB STUDY ON VOLATILES

- B T E X
- TRICHLOROETHANE
- ADD-ON - 3 OIL & GREASE SAMPLES

SLIDE 13

SAMPLE TYPES

- EFFLUENT
- SPIKED EFFLUENT [9.7-14. PPB]
- "BLANK" SURFACE WATER
- SPIKED SURFACE WATER [4.7-7.5 PPB]
- ST. CLAIR RIVER WATER

SLIDE 14

METHODOLOGY

- VIALS INDIVIDUALLY SPIKED
- DISPENSING: FROM A BAKED DISPENSING BOTTLE
- ALL SOLUTIONS KEPT AT < 8°C
- 5 RANDOM SAMPLES – ANALYZED INTERNALLY
- 16 LABORATORIES
- MOST RESULTS WERE "ND"
  - -- EFFLUENT
  - -- SPIKED EFFLUENT
  - -- "BLANK" WATER
  - -- ST. CLAIR RIVER WATER

SLIDE 15

SPIKED EFFLUENT

	SPIKED	MED	FOD
BENZENE	7.4	ND	3/9
E. BENZENE	4.7	ND	1/9
TOLUENE	11.2	ND	1/9
XYLENE	14.0	ND	3/9
1,1,1 TCE	4.7	4.1	6/7

SLIDE 16

SPIKED WATER

	SPIKE	MEAN	SD
BENZENE	4.7	4.5	1.3
E. BENZENE	0	ND	–
TOLUENE	4.7	4.6	3.3
XYLENE	7.5	4.8	2.9
1,1,1 TCE	5.6	4.2	1.9

SLIDE 17

MOST COMMON "FALSE" POSITIVES

- BENZENE
- XYLENES
- CHLOROFORM
- METHYLENE CHLORIDE

SLIDE 18

CONCEPT OF PQL

- DEFINED: LIMIT AT WHICH 80% OF LABS OBTAIN RESULTS WITHIN ±40% OF TRUE VALUE
- 3 OTHER STUDIES SHOW PQL >> MDL
- THIS STUDY CONFIRMS THESE FINDINGS

SLIDE 19

FURTHER RECOMMENDATIONS

- STUDY BIODEGRADATION (AND USE OF PRESERVATIVES)
- STUDIES AT HIGHER SPIKE LEVELS TO OBTAIN VALID PQL'S

ENVIRONMENT ONTARIO INTERLABORATORY STUDIES PROGRAM

Sylvia Cussion
Quality Assurance Office
Laboratory Services Branch

ENVIRONMENT ONTARIO
INTERLABORATORY STUDIES PROGRAM



- Overview of MOE Program
- Individual Study Design
- Examples from Past Studies:
  - 88-1
  - Resin & Fatty Acids (Collaborative Studies)
  - 89-1
- Announcement of 90-1

ENVIRONMENT ONTARIO
INTERLABORATORY STUDIES PROGRAM



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INTERLABORATORY STUDY OBJECTIVES



- Assess and promote good laboratory practices
- Evaluate data comparability between Ontario environmental laboratories
- Collaborative study to assess a new method

1989 MOE INTERLABORATORY STUDIES



- 89-1: Volatile Organics & Solvent Extractables (MISA Groups 16, 17, & 25)
- 89-2: Resin & Fatty Acids (Collaborative Study) (MISA Groups 26 & PP3)
- 89-3: Dioxins in Water & Effluents *
- 89-4: Dioxins in Ambient Air *
- 89-5: Acid & Base/Neutral Extractables (MISA Groups 19, 20 & 23)
- 89-6: Metals, Total Nutrients & Phenols by 4-AAP (MISA Groups 9, 4, 6, 14, IS1, M5, MC1 & E1)

* Studies initiated by Dioxin Unit, LSB

ENVIRONMENT ONTARIO
INTERLABORATORY STUDIES PROGRAM



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  - Resin & Fatty Acids (Collaborative Studies)
  - 89-1
- Announcement of 90-1

INDIVIDUAL STUDY DESIGN



Select Parameters/Matrices
(Based on data quality issues of concern)

↓

Send Out Notification
3-4 weeks prior to sample distribution

↓

Prepare Samples

↓

Distribute Samples
Via courier

↓

Participants Report Results
(4 - 6 weeks)

↓

Data Entry by Lab Code

↓

Table(s) of Results to Participants
(Within 8 weeks)

↓ ↑

Corrections (if necessary)

↓

Final Report

U.S. CUSTOMS REQUIREMENTS



CONTENTS: Water Samples

WEIGHT: xx lb.

COUNTRY OF ORIGIN: Canada

DOLLAR VALUE: Less than $1.00

REASON FOR SHIPPING: Research Samples

DESTINATION: xxxx

ORIGINATOR: xxxx

INDIVIDUAL STUDY DESIGN



Select Parameters/Matrices
(Based on data quality issues of concern)

↓

Send Out Notification
3-4 weeks prior to sample distribution

↓

Prepare Samples

↓

Distribute Samples
Via courier

↓

Participants Report Results
(4 - 6 weeks)

↓

Data Entry by Lab Code

↓

Table(s) of Results to Participants
(Within 8 weeks)

↓ ↑

Corrections (if necessary)

↓

Final Report

INTERLABORATORY STUDY REPORT FORMAT



Summary & Conclusions

Introduction

Procedure

Results & Discussion

References

Appendices

ENVIRONMENT ONTARIO
INTERLABORATORY STUDIES PROGRAM



- Overview of MOE Program
- Individual Study Design
- Examples from Past Studies:
  - 88-1
  - Resin & Fatty Acids (Collaborative Studies)
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ENVIRONMENT ONTARIO
INTERLABORATORY STUDIES PROGRAM



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  - 89-1
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RESIN & FATTY ACIDS COLLABORATIVE STUDIES



88-2A: Ampoules for Spiking Reagent Water and Direct Methylation

88-2B: Ampouled Standards in Two Different Solvents for Direct Methylation and Instrumental Injection

88-3: Spiked Samples Prepared in Reagent Water and Pulp & Paper Mill Effluents

89-2: Spiked Samples Prepared in Reagent Water and Pulp & Paper Mill Effluents

ENVIRONMENT ONTARIO
INTERLABORATORY STUDIES PROGRAM



- Overview of MOE Program
- Individual Study Design
- Examples from Past Studies:
  - 88-1
  - Resin & Fatty Acids (Collaborative Studies)
  - 89-1
- Announcement of 90-1

ENVIRONMENT ONTARIO
INTERLABORATORY STUDIES PROGRAM



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  - 88-1
  - Resin & Fatty Acids (Collaborative Studies)
  - 89-1
- Announcement of 90-1

MOE INTERLABORATORY STUDY 90-1



PARAMETERS: Total cyanides (MISA Group 2)

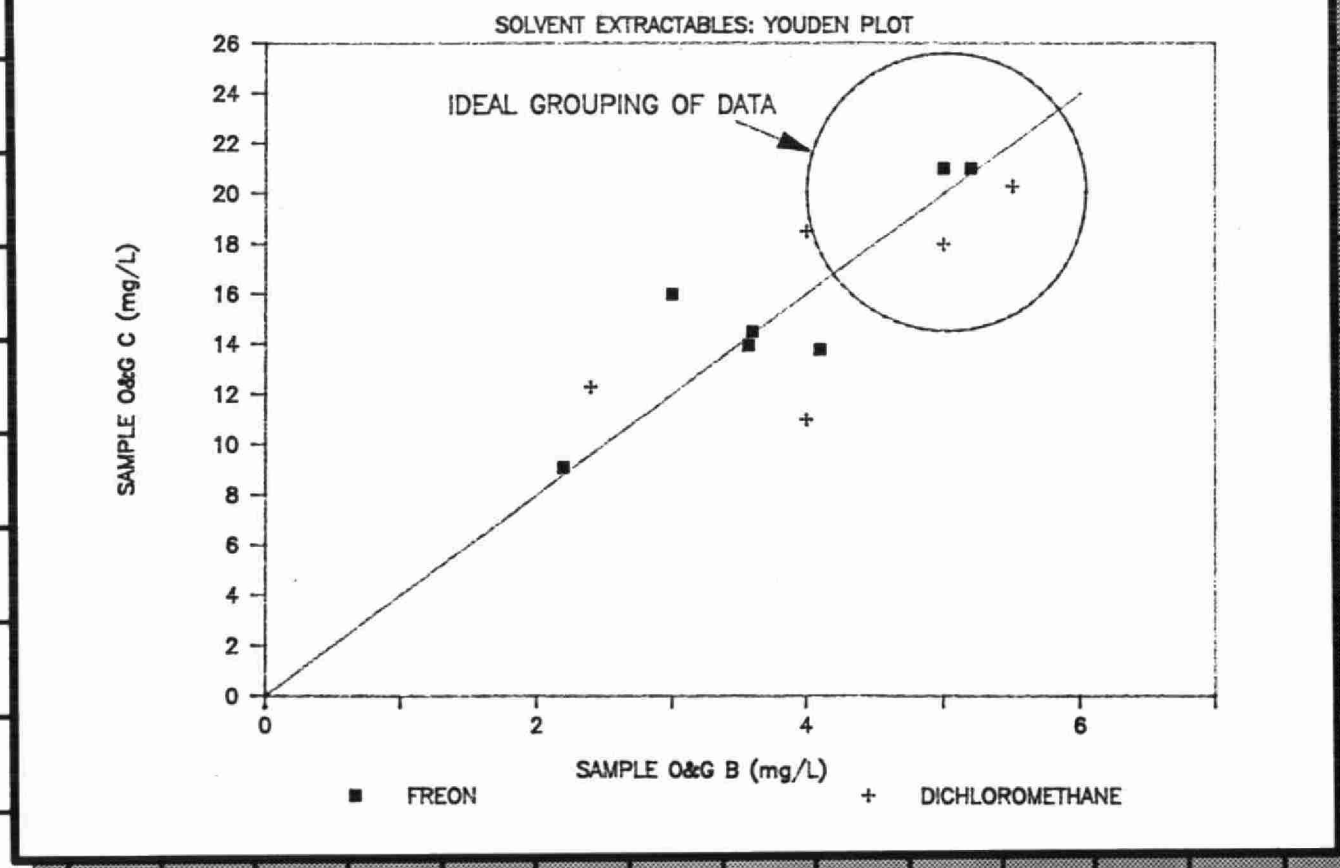
NOTIFICATION: Week of Dec. 4, 1989

SAMPLE DISTRIBUTION: Week of Jan. 15, 1990

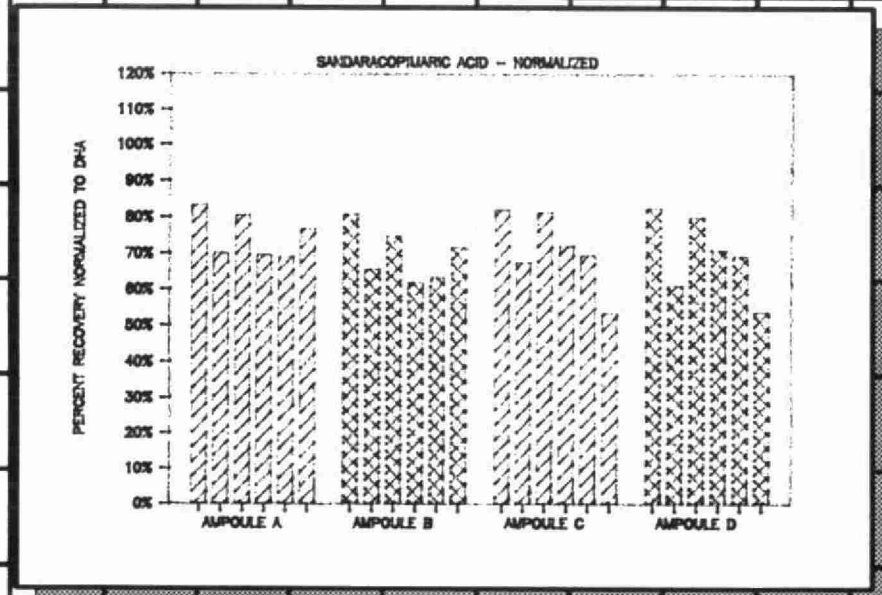
MATRICES: Reagent water and mixed effluent

NUMBER OF SAMPLES: 4 of each (total = 8)

FIGURE 10: INTERLABORATORY STUDY 89-1



INTERLABORATORY STUDY 88-2A
FIGURES 3 AND 3A:



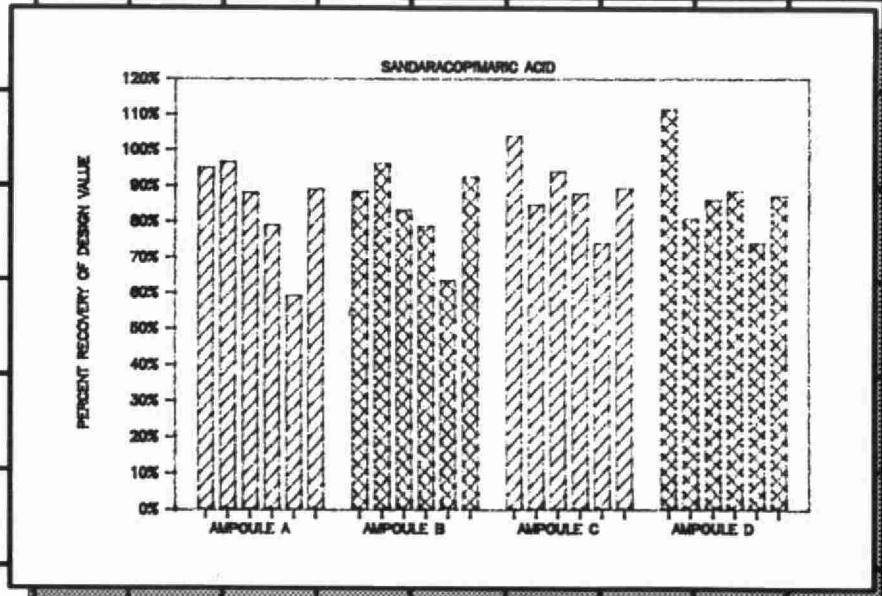


FIGURE 3: INTERLABORATORY STUDY 89-1

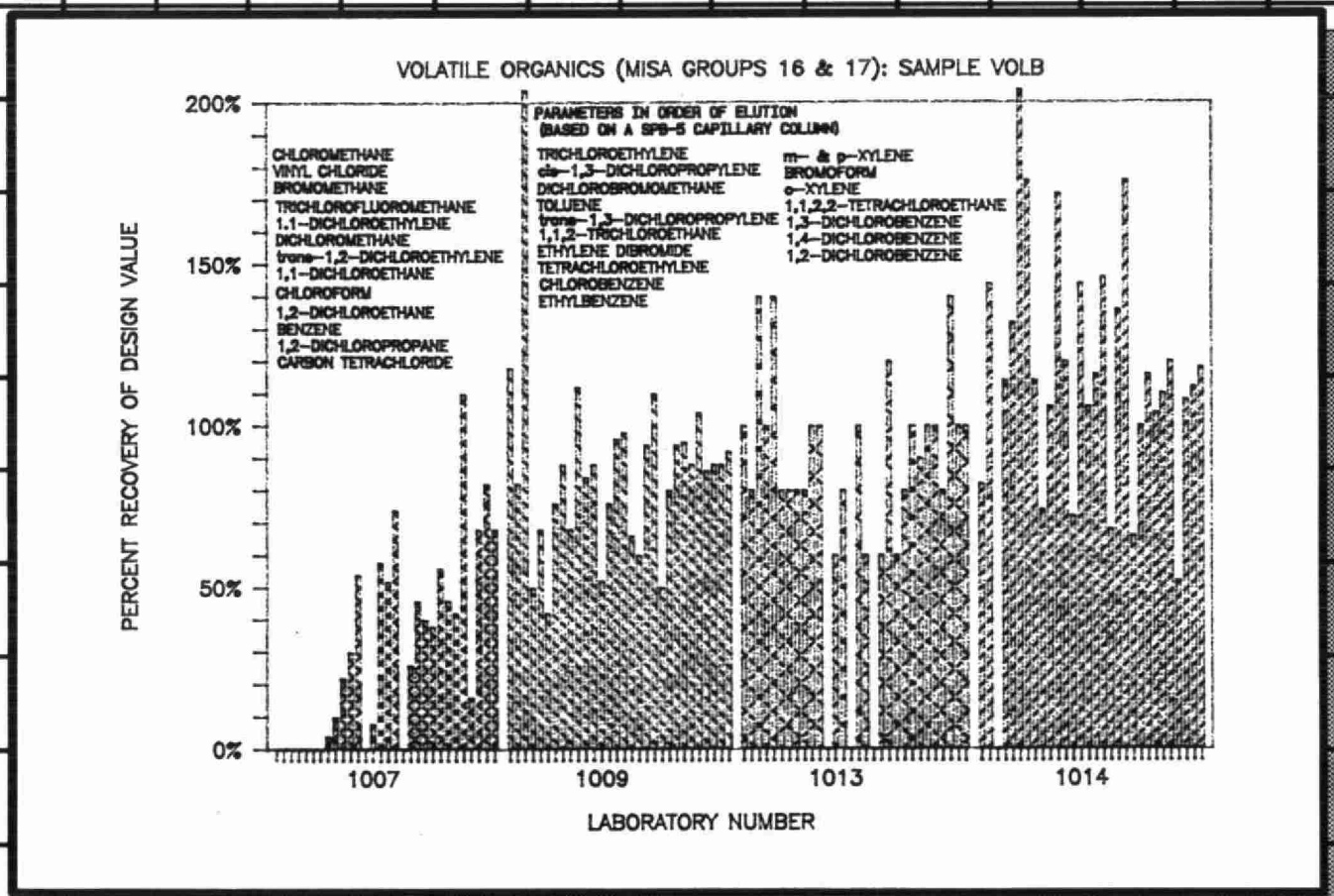


FIGURE 5: INTERLABORATORY STUDY 89-1

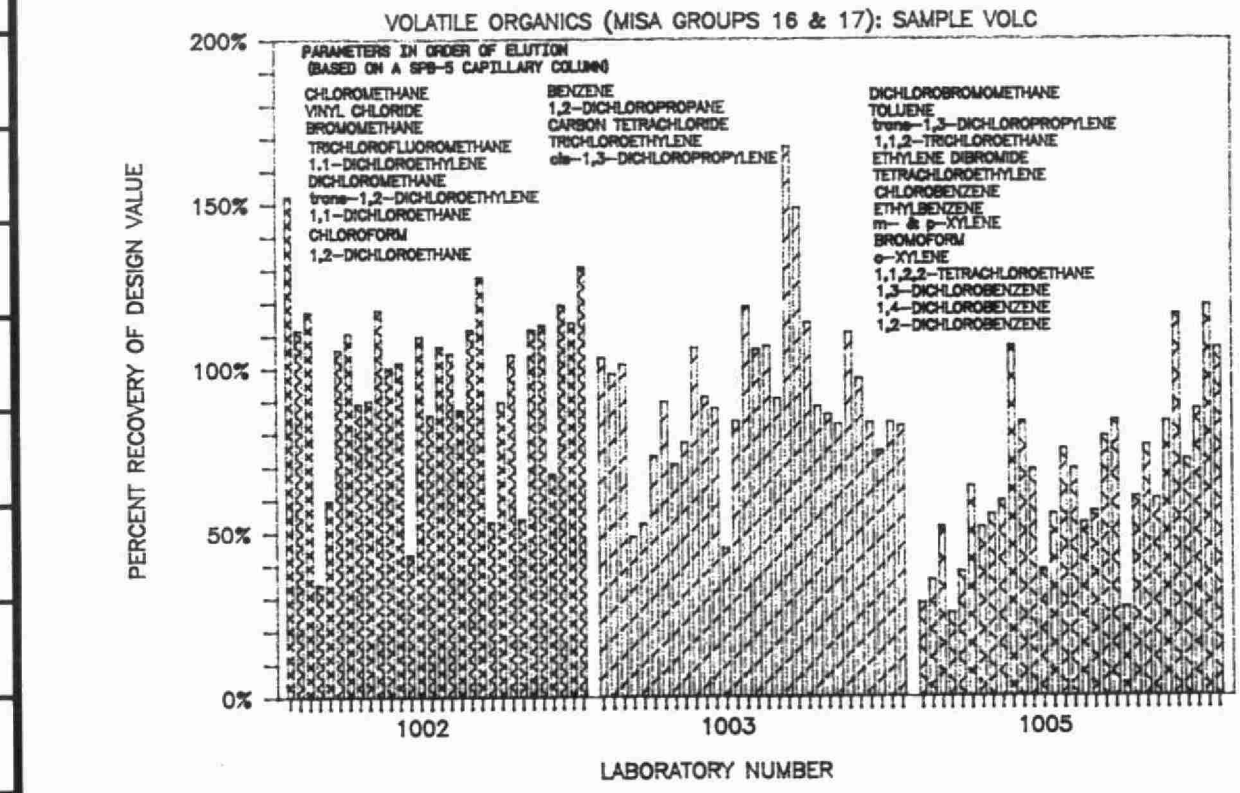


FIGURE 1: ROUND ROBIN 88-1; VOLATILES

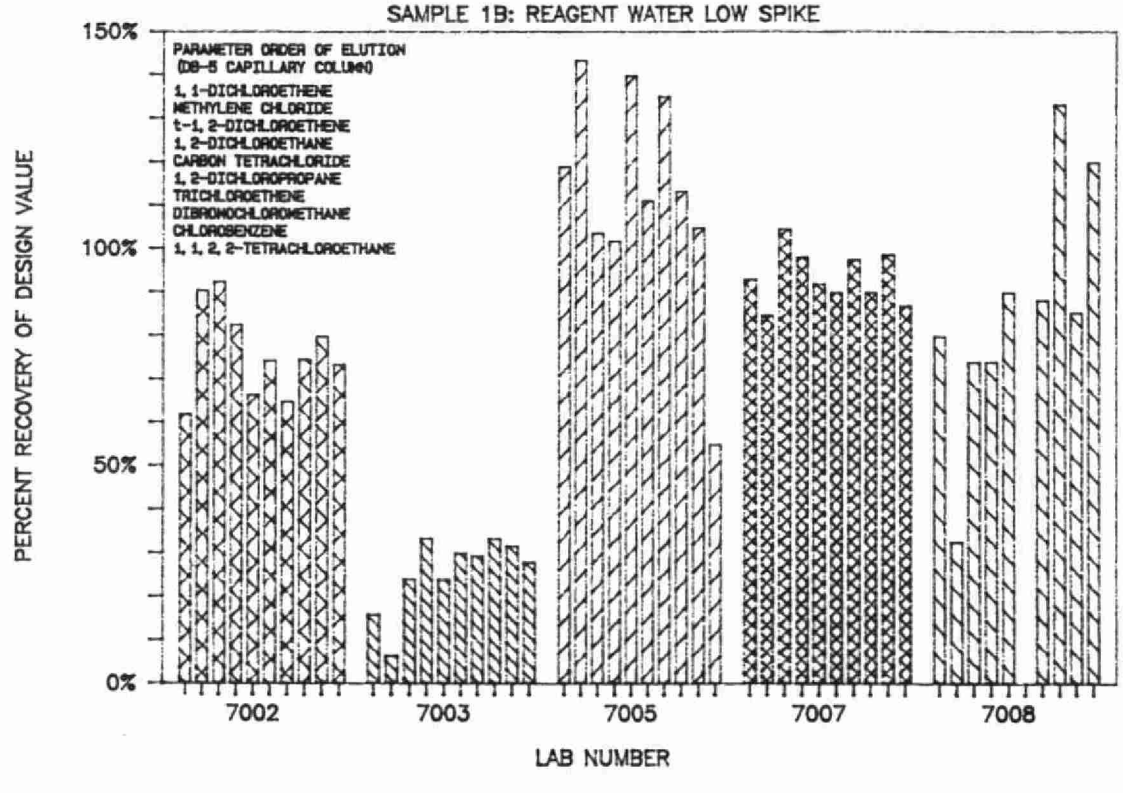


FIGURE 11: ROUND ROBIN 88-1; BASE/NEUTRAL

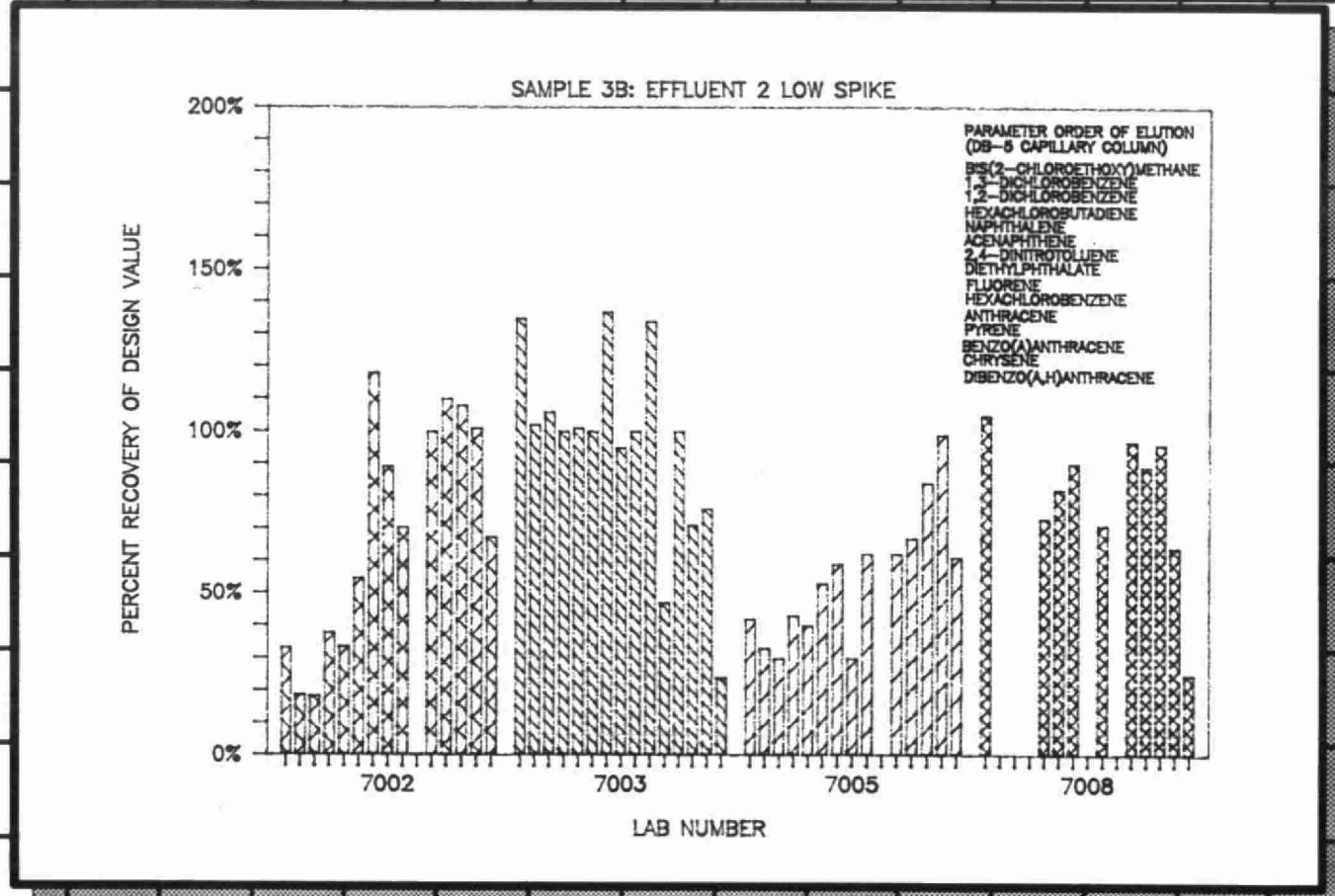
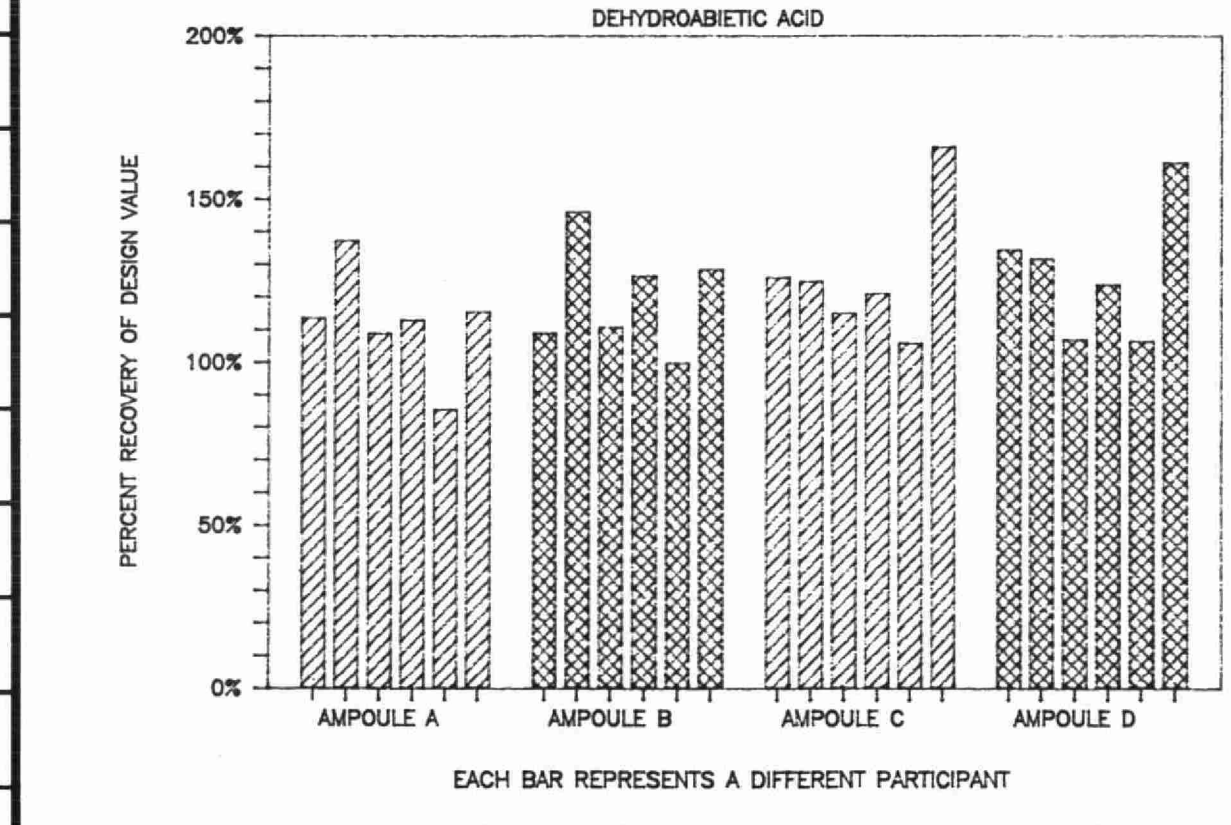


FIGURE 11: INTERLABORATORY STUDY 88-2A



SECTION FIVE - Work Group Reports

SECTION FIVE

SESSION ONE - WORKGROUP REPORTS

WORKGROUP 1 - ROUTINE CHEMISTRY 1

2 - ROUTINE CHEMISTRY 2

3 - ROUTINE CHEMISTRY 3

4 - INORGANIC 1 + 2

5 - ORGANICS 1 + 2

6 - ELEMENTAL SCAN

7 - OPEN CHARACTERIZATION (ORGANICS)

NOTE: THESE REPORTS REPRESENT THE SUMMARY COMMENTS OR HIGHLIGHTS PRESENTED BY THE AD-HOC SPEAKERS. PARTICIPANTS FROM INDIVIDUAL WORKGROUPS ARE ENCOURAGED TO REVIEW THEIR OWN NOTES TAKEN DURING DETAILED CONVERSATIONS AND TO USE THESE HIGHLIGHT REPORTS AS TRIGGERS TO ITEMS OF INDIVIDUAL CONCERN. MOE STAFF WILL USE THE IDEAS AND ADDRESS CONCERNS EXPRESSED IN FUTURE WORKSHOP PLANS.

MISA LABORATORIES ANALYTICAL WORKSHOP

GROUP DISCUSSIONS ACTIVITIES

- Workshop success depends on your participation
- Raise questions; provide solutions, alternatives
- Not a Ministry lecture
- Time factors:

  15 Minutes Refreshments

  60 Minutes Group Discussion

  15 Minutes Wrap–Up (Presentation Preparation on Overheads)

MISA LABORATORIES ANALYTICAL WORKSHOP

GROUP DISCUSSIONS ACTIVITIES

- Discussions will be facilitated by Environment Ontario Laboratory Staff
- Reporting Secretary will be nominated
- Brief notes to be prepared for 5 minute presentation by Reporting Secretary (Preformated transparencies to be used)

MSA LABORATORIES ANALYTICAL WORKSHOP

GROUP DISCUSSIONS ACTIVITIES

Smaller Group Discussions on:

- Conventionals
- Inorganics
- Organics
- Organic Characterization
- Elemental Characterization

Registration Badge indicates chosen group

WORKGROUP 1 - ROUTINE CHEMISTRY 1

AD HOC PRESENTATION BY: MR. JOE CATELLA - ENVIROCLEAN

A. TOPICS DISCUSSED

- o PHENOLS METHOD
- o SULPHIDE METHOD
- o CYANIDE METHOD
- o ION CHROMATOGRAPHY VS. ION SELECTIVE ELECTRODES
- o QA/QC - CONTROL CHART REQUIREMENTS/PROTOCOLS
  - METHOD DETECTION LIMITS (MDL)

B. ISSUES RESOLVED

- o REGULATION MDL CAN BE DEVELOPED IN A NUMBER OF FASHIONS, THE ONLY REQUIREMENT IS TO MEET OR EXCEED (GET LOWER THAN) THE REGULATORY VALUE BY ANY METHOD THAT ADHERES TO PRINCIPLES AND PROTOCOLS.
- o REGULATORY VALUES HAVE AN UNCERTAINTY FACTOR OF 1.6.

C. ISSUES OUTSTANDING

- o NOTHING IS "CUT AND DRY".
- o AVAILABILITY, PREPARATION AND STABILITY OF STANDARDS FOR:
  - CYANIDE
  - PHENOLS

WORKGROUP 2 - ROUTINE CHEMISTRY 2

AD HOC PRESENTATION BY:

PETER WILSON, MOE

A. TOPICS DISCUSSED

CHEMISTRY 2

- o METHODS FOR: DOC, TOC, NH_3 (PROBE), PHENOLICS
- o OIL AND GREASE
- o AUTOMATED VS MANUAL METHODS
- o NIMMP
- o AVAILABILITY OF REFERENCE MATERIALS

B. ISSUES RESOLVED

- o DOC AND TOC
  METHODS ARE MATRIX SPECIFIC

C. ISSUES OUTSTANDING

- o SOURCES OF REFERENCE MATERIALS

WORKGROUP 3 - ROUTINE CHEMISTRY 3

AD HOC PRESENTATION BY:

DAVE SPONG - DOFASCO

A. TOPICS DISCUSSED

CHEMISTRY 3

- o QUALITY CONTROL
- o MDLs
- o BOD
- o TRC
- o TSS/VSS
- o NIMMP
- o SULPHIDE
- o QC SAMPLES MUST BE CARRIED OUT WITH EVERY RUN
- o MDLs IDENTIFIED AS A PERFORMANCE CAPABILITY NOT A ROUTINE SAMPLE ANALYTICAL CAPABILITY.
- o TRC CAN BE PERFORMED BY ANY RECOGNIZED METHOD THAT COMPLIES WITH PRINCIPLES AND PROTOCOLS.
- o SULPHIDE SAMPLES - FILTER AFTER COLOUR DEVELOPS
- o NIMMP - WAIT FOR NEW REGULATION TO CONTRIBUTE NEW METHODS <u>BUT</u> START NOW

B. ISSUES RESOLVED

ISSUES OUTSTANDING

C.

- o DIFFICULTIES OF REPLICATES FOR OIL AND GREASE
- o TRC HOLDING TIME
- o AVAILABILITY OF STANDARD REFERENCE MATERIALS

WORKGROUP 4 - INORGANIC 1 AND 2

AD HOC PRESENTATION BY:

DR. OTTO HERRMANN - ONTARIO HYDRO

A. TOPICS DISCUSSED

- o ALTERNATE SAMPLE PREPARATION TECHNIQUES
- o ALTERNATE METHODS (NIMMP)
- o SOURCE AND USE OF STANDARDS MATERIALS
- o ELEMENTAL SCAN MDL EXCUSIONS (I.E. MISSING 102 MDL OUT OF 70)
- o REGULATION REQUIREMENTS FOR DOCUMENTATION
- o PERFORMANCE MANAGEMENT (ROUND ROBINS, CHECK STANDARDS) BY THE MINISTRY OF THE ENVIRONMENT

B. ISSUES RESOLVED

- o IF AN ANALYTICAL APPROACH (SAMPLE PREP OR INSTRUMENTAL ANALYSIS) IS NOT SPECIFICALLY EXCLUDED BY THE MISA REGULATIONS AND CONFORMS TO THE PRINCIPLES AND PROTOCOLS SPECIFIED - DO IT!
- o STANDARDS USED FOR CALIBRATION CAN BE EITHER COMMERCIALLY OBTAINED OR DEVELOPED IN-HOUSE BUT MUST BE VERIFIED FOR ACCURACY AND IDENTIFY AGAINST AT LEAST ONE OTHER EXTERNAL STANDARD INCLUDING THOSE PROVIDED BY N.I.S.T.

C. ISSUES OUTSTANDING

- o NIMMP A) NEED TO BE ABLE TO APPLY FOR MINOR OR MUTUALLY (IE. MOE, INDUSTRY, LABORATORY) AGREEABLE CHANGES RAPIDLY
  B) NEED TO BE ABLE TO ADDRESS SAMPLE PREPARATION AND INSTRUMENTAL MEASUREMENT CHANGES INDIVIDUALLY
- o NEED TO CLARIFY DATA ARCHIVING REQUIREMENTS IN REGULATION
- o MOE PROVISION OF CHECK STANDARDS (NOT CURRENT POSSIBLE)
- o MDL EXCURSIONS OF 1 OR 2 ELEMENTS AND OF A GROUP OF MANY

WORKGROUP 5 - ORGANICS 1 + 2

AD HOC PRESENTATION BY: DR. DAVID HALL - MOE

A. TOPICS DISCUSSED

- o MDLs APPROACHES TO DEVELOPING UNCERTAINTY OF VALUES, USE OF LARGER SAMPLES
- o ALTERNATE METHOD FOR VOLATILES (I.E. USE OF FID)
- o STORAGE TIME REQUIREMENTS
- o QUALIFYING DATA WITH REMARKS CODES
- o INTERLABORATORY STUDIES
- o REPORTING OF CORRECTED AND UNCORRECTED DATA (I.E. BLANK CORRECTION)
- o DIOXINS ANALYSIS

B. ISSUES RESOLVED

- o MDLs
  - A) DEVELOP IN GROUPS AS APPROPRIATE TO LAB OPERATIONS OR ACCORDING TO MISA TEST GROUPINGS
  - B) RECOGNITION THAT MDL IS A PERFORMANCE CRITERIA FOR ALL LABS; A LOW LEVEL TARGET FOR ROUTINE SAMPLES BUT NOT ALWAYS ATTAINABLE DUE TO MATRIX INTERFERENCES
  - C) SECTOR SPECIFIC MDLS (E.G. AOX) WILL BE IN INDIVIDUAL SECTOR REGULATIONS.
- o VOC METHOD DOES IDENTIFY FID FOR NON-CHLORINATED (ATG#16)
- o STORAGE TIMES MUST BE DOCUMENTED, DUE DILIGENCE MUST BE SHOWN
- o MIDES DOES INCLUDE A RANGE OF REMARKS CODES TO ALLOW ANALYSTS TO QUALIFY THEIR DATA
- o INTERLABORATORY STUDIES ARE DISCUSSED IN SECTION 4

C. ISSUES OUTSTANDING

- o MOST OUTSTANDING ISSUES WERE RELATED TO DATA USE AND INTERPRETATION WHICH WILL BE ADDRESSED DURING JOINT DEVELOPMENT OF LIMITS REGULATION

Workgroup 6 - Elemental Scan

Ad Hoc Presentation by:

A. Topics Discussed

- o Detection Limits; effects of interferences
- o Relationship of complimentary data from ATG#9
- o Background Corrections/Spectral Interferences
- o Source and traceability of standard reference materials (SRMs)

B. Issues Resolved

- o MDLs are independent of determinate error; routine sample analysis can be accompanied by qualifiers to identify interferences or matrix problems
- o Background corrections and interferences must be accommodated by method protocols and be corrected for or data reported be qualified
- o There must be a clear audit trail to SRMs or, in their absence/unavailability, the next best available reference material

C. Issues Outstanding

- o Relationship and use of complimentary data (possibly conflicting?) from other elemental analysis
- o SRMs - Provision by MOE of either
  - A) mixed standards or
  - B) list of potential suppliers

WORKGROUP 7 - OPEN CHARACTERIZATION (ORGANICS)

AD HOC PRESENTATION BY: MR. TERRY COOPER - ORTECH

A. TOPICS DISCUSSED

- o REPORTING FORMAT
- o USE OF INTERNAL STANDARDS
- o MDL GUIDELINES FOR DIFFERING MATRICES
- o COMPOUND CLASS LEVEL IDENTIFICATIONS
- o CHOICES AVAILABLE IN ANALYTICAL INSTRUMENTS

B. ISSUES RESOLVED

- o MOCHA REPORTING FORMAT
- o MANDATORY VERSUS OPTIONAL REQUIREMENTS FOR CHARACTERIZATION

C. ISSUES OUTSTANDING

- o IDENTIFICATION OF NEED FOR MORE SKILLED ANALYSTS
- o VARIABLE DETECTION LIMITS FOR DIFFERENT MATRICES (CAN BE ACCOMMODATED BY QUALIFYING REMARKS CODES)
- o NEED TO IMPROVE THE REGULATORY EVALUATION PROCESS IN ESTABLISHING MDLS, PERFORMANCE STANDARDS

(7772)
QD 79/Q35/M57/1989/MOE MISA

Date Due

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Ontario Ministry of the En
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quality assurance ammt
c.1 a aa

Produced By: Environmental Training Institute